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NITROGEN COMPOUNDS IN HYDROTREATED GAS OIL FROM ATHABASCA BITUMEN

by

PAULA JOKUTY

(C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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June 19, 1992

DEDICATION

for my family

ABSTRACT

A retention chromatographic method was used to concentrate nitrogen compounds in hydrotreated synthetic crude oil. Over 90% of the nitrogen compounds were recovered when a sample to sorbent ratio of 2:1 was used. A ratio of 9:1 resulted in 60% recovery, but with better enrichment of specific nitrogen types in the two fractions collected. The most abundant neutral nitrogen compounds were alkyl-substituted carbazoles substituted with one to fifteen carbons. ^{13}C-NMR and infrared spectroscopic analysis showed that the dominant isomers were substituted at the 4-position on the carbazole ring system. The most abundant basic nitrogen compounds were 5,6,7,8-tetrahydroquinolines and octahydrobenzoquinolines. The largest GC peaks due to individual components were from alkylpyridines and alkyltetrahydroquinolines. Higher ring systems were also found. ^{13}C- and ^{1}H-NMR spectroscopy indicated a high degree of substitution but with protons frequently found in the position *meta* to the nitrogen. The distribution and degree of substitution of product ring types were consistent with a multistep mechanism for hydrodenitrogenation, including hydrogenation of carbon rings followed by cracking of the hydrogenated rings to give alkyl pyridines. This mechanism of hydrodenitrogenation is significantly different from that reported for quinoline.

Infrared spectroscopy and GC-mass spectrometry were used to analyze the structural characteristics of solvent extracts from spent hydrotreating catalysts. Furans, benzofurans, phenanthrenes, and octahydrobenzocarbazoles were found. These were likely to have originated in the feed oils. Methyl esters and aromatic hydroxy compounds were also identified, but these are likely to be oxidation products from exposure to air.

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Chapter 1

Introduction

As world reserves of conventional crude oil dwindle, processing of heavier feeds grows in importance. These heavier feeds contain more aromatic nitrogen compounds than their lighter counterparts. Polar nitrogen compounds have been studied for many years as poisons for cracking catalysts (Mills *et al.*, 1950) and as contributors to sludge formation in distillate products (Batts and Fathoni, 1991). The development of heavy and synthetic crude oils has, therefore, generated a great deal of interest in the chemistry and kinetics of hydrodenitrogenation.

Crude oils contain two main types of nitrogen compounds: the basic pyridine benzologs and the neutral pyrrole benzologs. Bitumens contain similar nitrogen compounds; for example, Frakman *et al.* (1987) identified basic pyridine benzologs in maltenes from Athabasca bitumen, and pyrrole benzologs were found in the maltene and asphaltene fractions (Mojelsky *et al.*, 1986; Payzant *et al.*, 1985).

Much less attention has been paid to the nature of the nitrogen compounds which remain after hydroprocessing of distillate fractions. Typical gas oils contain 200-1000 ppm of nitrogen, so that conventional liquid chromatographic separation gives only a few milligrams of purified nitrogenous extract. Consequently, Dorbon *et al.* (1984) and Ignatiadis *et al.* (1986) relied on GC retention times and mass spectrometry for identification of alkylcarbazoles and benzocarbazoles in coker gas oil, because other spectroscopic methods were not practical.

Although the detrimental effects of heteroatoms on catalysts have long been recognized, relatively little work has been done to determine which compounds are most poisonous (Mills *et al.*, 1950; Dorbon *et al.*, 1984), or which compounds are actually present on the surface of a spent catalyst (Choi and Gray, 1988; Choi and Gray, 1991).

The main objectives of this research were:

1. The recovery of gram quantities of nitrogenous material from a hydrotreated coker gas oil by a novel chromatographic method.
2. The characterization of the recovered compounds.
3. Structural analysis of material extracted from spent hydrotreating catalysts.

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Chapter 2

Neutral Nitrogen Compounds in Hydrotreated Gas Oil from Athabasca Bitumen[1]

INTRODUCTION

Crude oils contain two main types of nitrogen compounds: the basic pyridine benzologs and the neutral pyrrole benzologs, and 20-30% of the nitrogen appears in the pyrrole compounds (McKay *et al.*, 1976). Bitumens contain similar nitrogen compounds; for example, pyrrole benzologs were found in the maltene and asphaltene fractions of Athabasca bitumen(Mojelsky *et al.*, 1986; Payzant *et al.*, 1985).

Much less attention has been paid to the nature of the nitrogen compounds which remain after hydroprocessing of distillate fractions. Dorbon *et al.* (1984) identified a series of alkylcarbazoles and benzocarbazoles in a coker gas oil. The benzocarbazoles were converted more than carbazoles at 10 MPa and 360 °C, while the opposite was observed at 380 °C and 5 MPa. Ignatiadis *et al.* (1986) detected highly resistant alkylcarbazoles in a hydrotreated coker gas oil. The resistance of these compounds to conversion at 360 °C and 7 MPa was attributed to the position of the alkyl substituents on the aromatic nucleus.

These results indicate that the activity of hydrodenitrogenation catalysts should be tested with the resistant alkylated isomers of the nitrogen compounds. In addition to detailed studies of specific isomers, methods for routine process monitoring are also required. Pyridinic nitrogen bases can be monitored by potentiometric titration in crude oils and coker distillates (Buell, 1967), but concentrations in hydrotreated products are too low for this method. Pyrrole compounds can be determined by FT-IR spectroscopy

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[1]A version of this chapter has been published. Jokuty, P. L. and Gray, M. R. *Energy & Fuels* **1991**, *5*, 792-795.

down to levels of about 0.5 mol/kg, using a solution of sample in methylene chloride (McKay *et al.*, 1976). Direct analysis of the nitrogenous extract provides a method for verifying these analyses.

The objectives of this study were to recover gram quantities of nitrogenous material from hydrotreated coker gas oil by a novel chromatographic method, to characterize the recovered compounds, and to verify the use of IR spectroscopy for more routine monitoring of pyrrolic compounds.

EXPERIMENTAL METHODS

Oil Sample

The oil was a hydrotreated coker gas oil, derived from Athabasca bitumen. The material had been hydrotreated in a commercial trickle-bed reactor over a Ni/Mo on γ-alumina catalyst, at a temperature of 360-400 °C and a pressure of 9.5-11 MPa.

Solvents

The pentane, methylene chloride and methanol solvents were HPLC grade, purchased from Fisher Scientific.

Retention Chromatographic Method

A glass 1m x 3cm (O.D.) chromatographic column fitted with a Teflon stopcock was used. Glass wool was used to retain the packing material. The column was packed with 400 ml (approximately 250 g) of 100-200 mesh silica gel (Terochem Laboratories Ltd.). The silica gel was dried overnight at 140 °C. The dry packing was added to the column slowly while tapping the column to ensure a uniform sorbent bed. The column was then flushed with pentane to remove trapped air from the packing. The column was kept saturated and covered with pentane until immediately before sample addition. At that

time the pentane level was dropped just to the surface of the silica gel and then the stopcock was closed.

250 ml of synthetic crude oil was poured into the column, taking care initially not to disturb the surface of the silica gel packing. The crude oil was allowed to drain by gravity and an additional 250 ml was added. The oil took several hours to pass completely into the silica gel. As the oil moved down into the silica gel, five distinct bands became apparent. At the front was a colourless band resembling a saturates fraction, distinguishable from the pentane in the column by a difference of refractive index which made it translucent. This band was followed by a similarly translucent yellow band with a green fluorescence, resembling an aromatics fraction. Next came an opaque brown band followed by a fluorescing black band and finally, at the very top of the column, a non-fluorescing black band. The colourless and yellow bands accounted for the bulk of the sample volume, and could be seen moving downward at the same rate that the pentane was being displaced. The brown band moved much more slowly and the black bands did not appear to move at all. The column had to be turned off overnight and by the next morning the divisions between bands had disappeared, leaving coloured zones with no distinct borders.

When the oil sample had completely entered the top of the silica gel packing the column was turned off momentarily and 250 ml of pentane was poured into the column. More pentane was added as required and the unretained oil was washed from the column and collected until only a very faint yellow colour could be seen in the eluant. A total volume of 1 - 2 litres of pentane was used.

As the last of the pentane entered the silica gel, 250 ml of methylene chloride were added to the column. The stopcock was opened and the methylene chloride extraction was begun. As the methylene chloride entered the silica gel, a distinct reddish-brown front could be seen moving downwards. More methylene chloride was added as needed. When

this front reached the stopcock, collection of the unretained oil was deemed complete and collection of the methylene chloride extracted fraction began. Approximately 500 ml methylene chloride were used; the final methylene chloride eluting from the column was colourless. The methanol extraction was then carried out in similar fashion, using about 750 ml of methanol. As the methanol moved through the silica gel, it removed the dark brown colour remaining after the methylene chloride extraction.

The bulk of the solvents collected with the unretained oil and the two solvent extracted fractions was removed by rotary evaporation. The two extracts were then transferred to evaporating dishes and the remaining solvent was removed by placing the dish on a warm heating mantle in a fumehood. The solvents were considered to have been completely removed when a constant weight was obtained.

Analytical Methods

C, H, N and O content of the extracts were measured by the Microanalytical Lab, Chemistry Department, University of Alberta, using Perkin-Elmer 240 and 240B analyzers. S was determined in a Leco S-132 Sulfur Determinator. For the oil, C, H and S were determined as for the extracts, N was determined with an Antek pyroreactor and digital nitrogen analyzer.

Infrared spectra were recorded on a Nicolet 730 FTIR Spectrometer by co-adding 32 scans at a resolution of 4 cm^{-1}. The samples were dissolved in methylene chloride and run in 0.05 cm NaCl cells. ^{13}C NMR spectra were obtained with a 200 MHz Bruker WH-200 spectrometer. These spectra were collected by the personnel of the Nuclear Magnetic Resonance Laboratory, Chemistry Department, University of Alberta. ^{1}H NMR spectra were recorded with a Bruker WP-80 spectrometer. A GC-mass spectrum of the methanol extract was obtained using a fused silica DB-1 capillary column coupled to a Varian VG 7070E mass spectrometer. This work was performed by L. Harrower, Mass Spectrometry Laboratory, Chemistry Department, University of Alberta. A fused silica DB-1 column

(0.25 mm i.d. x 30 m) on a HP 5890 gas chromatograph was used with helium as carrier gas, with a flame-ionization detector. The temperature program was 170 °C for 2 minutes, then heating at 3 °C/min to a final temperature of 270 °C. Field-ionization mass spectroscopy was performed by SRI International, Menlo Park, CA (U.S.A.). GC-FTIR was performed in the Spectral Services Laboratory, Chemistry Department, University of Alberta, on a Hewlett-Packard HP5765 IRD using a Supelco Ultra 2 column.

The gas chromatographic analysis (HP Model 5710A, TC detector) of the boiling point distribution of the oil and the two extracts was carried out using a 2 ft x .125 in (o.d.) column of 10% UCW 982 on P-AW, 80-100 mesh. The column was heated at a uniform rate of 8 °C/min from -10 to 350 °C. The He carrier gas flow rate was 60 mL/min.

Potentiometric titration of basic nitrogen followed Buell (1967). 100-150 mg of sample was dissolved in 10 mL of benzene and 20 mL of either acetonitrile or acetic anhydride to measure strong bases and very weak bases respectively. The solution was titrated with 0.1 N perchloric acid in dioxane. A detailed description of the titration procedure is given in the Appendix.

RESULTS

Retention Chromatography Fractions

The retention chromatography technique was very effective for concentrating and removing the nitrogen-containing compounds from the oil. A balance on nitrogen showed that 90% of the nitrogen was recovered in the methylene chloride and methanol extracts. The remaining 10% was likely retained on the column as indicated by some residual colour at the top of the silica gel. A mass balance based on the pyrrolic nitrogen peak at 3460 cm^{-1} in the IR spectra gave 119% recovery, which was reasonable for a semi-quantitative analysis using an average extinction coefficient. The properties of the extracts are listed in

Table 2.1. Both the solvent extracts were enriched in oxygen, relative to the feed oil, and depleted in sulfur.

When the separation was performed with a higher (9:1) ratio of sample oil to silica gel, the methylene chloride and methanol fractions were more enriched in specific nitrogen types. At the higher sample to adsorbent ratio, the methylene chloride extract contained 3.8 wt% N, mainly as carbazoles, with only 15 mol% basic nitrogen types. In contrast the methanol extract contained 3.7 wt% N, of which 78% was basic nitrogen types, and no detectable carbazole.

Mass Spectrometry Analysis

Both solvent extracts produced field-ionization mass spectrometry (FIMS) spectra with a majority of odd-mass ions (Table 2.1), indicating that nitrogen compounds were dominant. Using the calculated average molecular weights and the elemental analyses, the molar formulae were $C_{22}H_{27}O_{.2}N_{.8}S_{.1}$ in the methanol extract and $C_{26}H_{30}O_{.1}N_{.6}S_{.1}$ in the methylene chloride extract. A representative FIMS spectrum of the odd-mass ions is shown in Figure 2.1. The two major series can be assigned the formulae $C_nH_{2n-15}N$, for alkylcarbazoles, and $C_nH_{2n-17}N$. The latter series appeared at higher molecular weights than the alkylcarbazoles, and the molecular formula was consistent with either alkyltetrahydrobenzocarbazoles (alkyl-THBC), or alkylacridines. Both extracts contained the same major homologous series, but the methanol extract was enriched in the two dominant series relative to the methylene chloride extract. Table 2.2 lists the major series of ions from FIMS of the two extracts.

The assignment of the odd peaks to alkylcarbazoles and alkyl-THBC was confirmed by high-resolution mass spectrometry and GC-MS. The major peaks in the high-resolution spectrum were in the range 208.1123-249.1519 and could be attributed to the M^+ and $(M-1)^+$ peaks from C_3-C_5 alkylcarbazoles and C_1-C_2 alkyl-THBC. GC analysis of the methylene chloride and methanol extracts showed a distinct series of peaks

consistent with a homologous series of substituted carbazoles. The less substituted members of the series (m/z=195, 209, 233; C_2-C_4 carbazoles) showed little fragmentation; in each case the base peak was the molecular ion and the only significant decomposition was loss of a CH_3 to give an even m/z fragment ion. The higher members of the series (>C_5 carbazoles) were more prone to fragmentation so that the base peak was 15-29 mass units smaller than the molecular ion, indication longer alkyl chains. A cross scan of the gas chromatogram for ions of mass 181, 195, 209 etc. (Figure 2.2) showed that a dominant isomer was present at each mass number, consistent with the appearance of a pseudo-homologous series.

Infrared Spectroscopy

The hydrotreated gas oil showed an absorption at 3500 cm^{-1}, corresponding to the N-H stretch of pyrrolic compounds. The methylene chloride and methanol extracts showed much stronger absorption here, and accounted for 119% of the original peak based on an average extinction coefficient of 7000 (L/mol cm) (Petersen *et al.*, 1971). The extracts also showed strong bands in the region 900-700 cm^{-1} indicating that the aromatic rings were not highly substituted. GC-FTIR analysis of the major components showed the N-H stretch at 3500 cm^{-1} and bands from 1600-1000 cm^{-1} which were consistent with substituted carbazoles. The region from 900-700 cm^{-1} gave peaks at 850 cm^{-1} due to C-H bending of isolated aromatic hydrogens, 800 cm^{-1} due to pairs of adjacent hydrogens, and at 740 cm^{-1} due to groups of 3 or 4 adjacent hydrogens on the aromatic ring. These assignments for substituted carbazole are consistent with IR data for aromatics (Pouchert, 1981) and substituted carbazoles (Katritzky and Wang, 1988). A typical GC-IR spectrum is illustrated in Figure 2.3. Table 2.3 lists the major GC peaks and the appearance of the bands in the range from 900-700 cm^{-1}. The alkyl substitution patterns were divided into types as follows:

Type I: One band, so all aromatic hydrogens are in adjacent groups of three or four.

Example isomers: 4-alkyl-, 4,5-dialkyl-

Type II: Two bands, so some aromatic hydrogens are in groups of two, and some are in groups of three or four.

Example isomers: 3,4-dialkyl-, 3,4,5-trialkyl

Type III: Three bands, so some aromatic hydrogens are in groups of three or four, some are in groups of two and some are isolated.

Example isomers: 3-alkyl-, 3,5,-dialkyl-

NMR Spectra

The ^{1}H-NMR spectrum was relatively featureless, due to the mixture of compounds in the extracts, whereas the ^{13}C-NMR spectrum showed sharp resonances due to abundant isomeric types. The aromatic portion of the ^{13}C-NMR spectrum of the methanol extract is shown in Figure 2.4. The resonances at 108 and 110 ppm were very unusual in spectra of hydrocarbon mixtures, and were assigned to the unsubstituted C_1 and C_8 carbons in carbazole, and equivalent carbons in indoles, benzocarbazoles, and tetrahydrocarbazoles. These resonances accounted for 1.2% of the total carbon in the sample. Depending on whether the carbazoles contained one or two of these 1,8-unsubstituted carbons, these compounds made up 13-26 mol% of the total sample. The same resonances were also observed in the methylene chloride extract, but were less resolved and only accounted for 0.9% of the total carbon.

The six-membered pyridine derivatives gave a broad band from 150-160 ppm, due to the two carbons in the aromatic ring adjacent to the nitrogen molecule. The lack of any sharp signals in this range showed that the basic nitrogen compounds were not composed of a limited number of isomers. This band of resonances accounted for 2.9% of the total carbon in the methanol extract and 2.7% of the methylene chloride extract. Given two

moles of carbon in this range per mole of compound, the NMR data indicated 32 mol% basic nitrogen compounds in the methanol extract and 21% in the methylene chloride extract.

The aliphatic range of the ^{13}C-NMR spectrum gave resonances at 20.9 ppm, due to isolated methyl groups on aromatic rings, and 19.9 and 18.9 ppm due to shielded methyl groups (adjacent to another methyl or alkyl group). These assignments were consistent with the limited data on NMR of substituted carbazoles (Ahond *et al.*, 1968; Katritzky *et al.*, 1988) and substituted indoles (Parker and Roberts, 1970). The lack of a strong signal in the range of 15-16 ppm eliminated the possibility of any significant methyl substitution in the 1- or 8-positions of carbazole.

DISCUSSION

The analytical data allow construction of the most abundant nitrogen isomers in the extracts. The alkylcarbazoles were present in the highest concentrations, accounting for 22% of the methanol extract (from FIMS). Some of these homologs were also predominant in fractions isolated by Payzant *et al.* (1985) from the maltenes of Athabasca bitumen, i.e. m/z = 209, 223, 237 etc. The GC-IR spectra showed that six of the compounds were disubstituted according to the Type III pattern, with alkyl groups on opposite aromatic rings (e.g. 1,6-dialkyl carbazole). Another five GC peaks showed the Type II scheme, where substitution was unlikely in the 1- or 8-positions, due to the absence of a signal at 15-16 ppm, and the presence of signals from the unsubstituted 1- and 8-position carbons.

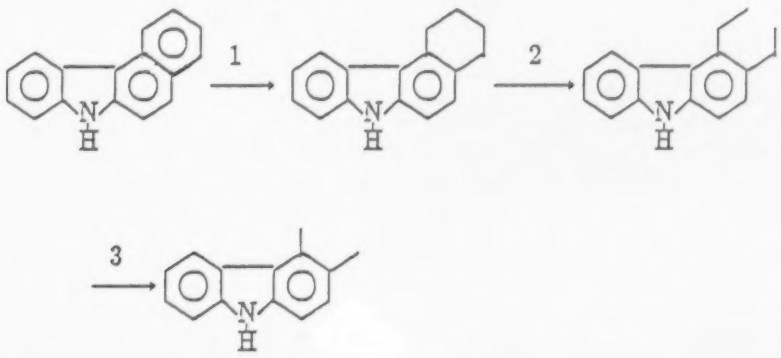
The combination of these requirements gave a limited number of possible isomers consistent with the data (Table 2.4). The spectroscopic techniques, especially NMR, average over the mixture. Hence other isomers cannot be ruled out, but the listing in

Table 2.4 is an appropriate starting point for further studies into the hydrodenitrogenation of resistant compounds.

The shift data of Parker and Roberts (1970) were used to estimate the NMR spectra of the substituted carbazoles, based on the assumption that the shifts in the aromatic carbons due to multiple substitution were additive. Comparison of this approach to the authentic spectrum of 1,4-dimethylcarbazole showed errors from 0.1 to 3.9 ppm in the predictions. The largest error was in estimating the shift of the substituted carbon in the 4-position. The estimated shifts indicated that the signal at 108 ppm could be assigned to a carbon in the 1-position para to an alkyl substituent (i.e. the 4-position), emphasizing the predominance of substitution in the 4- or 5-position of the ring. Note that in Table 2.4, four of the probable isomers have substituents in the 4- or 5-position. The predicted spectra for the aromatic carbons in the disubstituted carbazoles are shown in Figure 2.4. Given an uncertainty of ±1-2 ppm in these predicted spectra, a combination of the three isomers would plausibly account for most of the well-defined signals between 108 and 140 ppm.

The unusual persistence of carbazoles substituted in the 4-position was noted by Ignatiadis *et al.* (1986) in a study of hydrotreating of a coker gas oil. Dorbon *et al.* (1984) found that the carbazoles substituted in the 1-position were most reactive, which is consistent with their absence in the extracts from a hydrotreated sample. These previous studies observed a much different distribution of carbazole isomers than the present study. Their mixtures contained a number of methyl-substituted carbazole isomers, with one, two and three methyl groups. The present study, by contrast, indicates a prominent homologous series with substitution up to C_{12}-C_{15} (Figure 2.1). Such a distinct difference likely reflects the nature of the nitrogen compounds in the initial gas oils prior to hydrotreatment.

Although 4-alkylcarbazoles are clearly resistant to hydroprocessing, another factor contributing to their persistence could be the reaction pathway for conversion of higher ring number azole systems. A series of peaks consistent with both benzocarbazoles and tetrahydro benzocarbazoles was identified by FIMS (Table 2.2; Figure 2.1). Benzocarbazoles were identified in maltenes and asphaltenes from Athabasca bitumen by Payzant *et al.* (1985) and Frakman *et al.* (1987). Dorbon *et al.* (1984) and Ignatiadis *et al.* (1986) identified benzo[a]carbazole and benzo[c]carbazole in gas oil extracts on the basis of retention time. These observations suggest the following pathway, beginning in this case with benzo[c]carbazole:



In this scheme the tetrahydrobenzocarbazole forms by hydrogenation (Step 1), then cracks to give a C_4-carbazole, with a substituent in the 4-position. Further cracking (Steps 2 and 3) then gives the C_2-carbazole. The persistence of the C_2-carbazole would then be partly due to inherent resistance to conversion, and partly due to formation from higher ring compounds.

This study provides support for the use of infra-red spectroscopy as a semi-quantitative method for the analysis of pyrrolic nitrogen. Based on IR spectra, the concentration of pyrroles in the extracts was 0.092 mol/100 g. The FIMS data of Table 2.2 show that 23-50% of the total extract was made up of pyrroles, depending on how the series such as indole/quinoline are assigned. With an average molecular weight of 341, the

concentration of pyrrolic N was 0.067-0.15 mol/100 g. Titration of bases in the methanol extract in acetonitrile gave 0.09 equivalents/100 g, while the estimate from NMR was 32 mol% azines, or 0.1 mol/100 g. If this concentration of bases is subtracted from the total nitrogen concentration of 0.28 mol/100 g, then up to 0.18 mol/100 g of the methanol extract could be pyrrolic compounds. These other analyses, therefore, indicate reasonable consistence with the semi-quantitative estimate of pyrroles from infra-red spectroscopy.

CONCLUSIONS

1. The retention chromatography method gave 90% recovery of the nitrogenous compounds from gas oil, and provided gram quantities for subsequent analysis.
2. The major series of compounds extracted from the hydrotreated gas oil were alkylcarbazoles substituted with up to 15 carbons.
3. The major isomers were monoalkyl-, dialkyl-, and trialkyl-substituted carbazoles, with dominant substitution in the 4-position.
4. Infra-red spectroscopy gave a semi-quantitative analysis of pyrrolic nitrogen in the original gas oil which was consistent with the detailed analysis of nitrogenous extracts.

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Table 2.1

Analysis of Hydrotreated Gas Oil and Extracts

	Gas Oil	CH_2Cl_2 Extract	Methanol Extract	Total Extract
Yield, g		9.57	4.40	13.97
Yield, wt% of gas oil		2.10	0.97	3.07
Elemental Analyses				
C, wt%	87.64	88.04	85.62	
H, wt%	11.95	8.42	8.87	
O, wt%	0.02*	0.42	1.17	
N, wt%	0.09	2.32	3.59	2.72
S, wt%	0.30	0.80	0.75	
Boiling Fraction, vol%				
IBP-343 °C	45.2	4.4	2.4	
343-524 °C	54.5	95.3	92.9	
524 °C+	0.3	0.3	4.7	
Semi-Quantitative Analyses				
Pyrrolic N, by IR		0.092	0.092	0.092
Strong Bases			not done	0.090
Very Weak Bases			0.163	
FIMS Data				
Odd Mass Ions, mol%		56	75	69
Even Mass Ions, mol%		44	25	31
Average molecular weight		358	308	341

* Calculated from the oxygen content of the two extracts.

Table 2.2

Abundance of Homologous Series from FIMS

Ion Series[1]			Mol %[2]
Odd Series			
181-195-209-223-	Carbazole		15.7
207-221-235-249-	Tetrahydrobenzocarbazole, Acridine		12.8
173-187-201-215-	Indole, Quinolinone		7.8
175-189-203-217-	Benzocarbazole		7.1
191-205-219-233-	Pyridine		6.9
185-199-213-227-	Tetrahydrocarbazole, Quinoline		6.8
197-211-225-239-	Tetrahydroacridine		5.0
		Total	62.1
Even Series			
214-228-242-			6.1
216-230-244-	Benzofuran		5.8
212-226-240-			5.8
182-196-210-	Dibenzofuran		5.7
208-222-236-	Fluorenone		5.3
206-220-234-			4.8
218-232-246-			4.3
		Total	37.9

[1] The first peak for each series is at least 0.5% of the total extract.
[2] Mol % of the total methylene chloride + methanol extract, assuming unit response from FIMS.

Table 2.3

IR Bands from C–H Bending in Substituted Carbazoles

(from GC-FTIR spectra)

R.T., min	Band[1], cm^{-1}			Maximum # Alkyls	Substitution Type[2]
19.5	746			2	I
23.6	742	800		3	II
24.7	737	818		3	II
25.0	740	780	848	2	III
25.5	741	795		3	II
26.7	742	795	848	2	III
27.2	743	800		3	II
27.8	741	800	862	2	III
28.6	740	797	850	2	III
30.9	732	795	862	2	III
31.8	742	802		3	II
32.4	730	796	862	2	III

[1] IR bands are listed in order of decreasing intensity.

[2] The substitution types are as follows:

Type I: all aromatic hydrogens are in adjacent groups of 3 or 4.

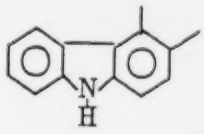
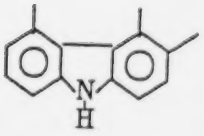
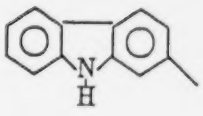
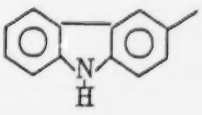
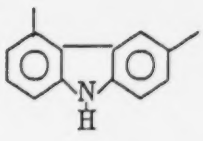
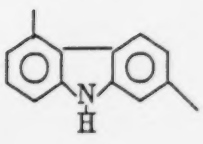
Type II: some aromatic hydrogens are in pairs, and some are in groups of 3 or 4.

Type III: some aromatic hydrogens are isolated, some are in pairs, and some are in groups of 3 or 4.

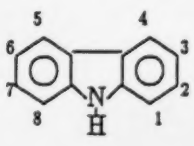
Table 2.4

Most Abundant Isomers of Alkyl Carbazoles

in Hydrotreated Gas Oil

Substitution Type		Methyl Isomer
Type II	3,4–dialkylcarbazole	
	3,4,5–trialkylcarbazole	
Type III	2–alkylcarbazole	
	3–alkylcarbazole	
	3,5–dialkylcarbazole	
	2,5–dialkylcarbazole	

Carbazole numbering:



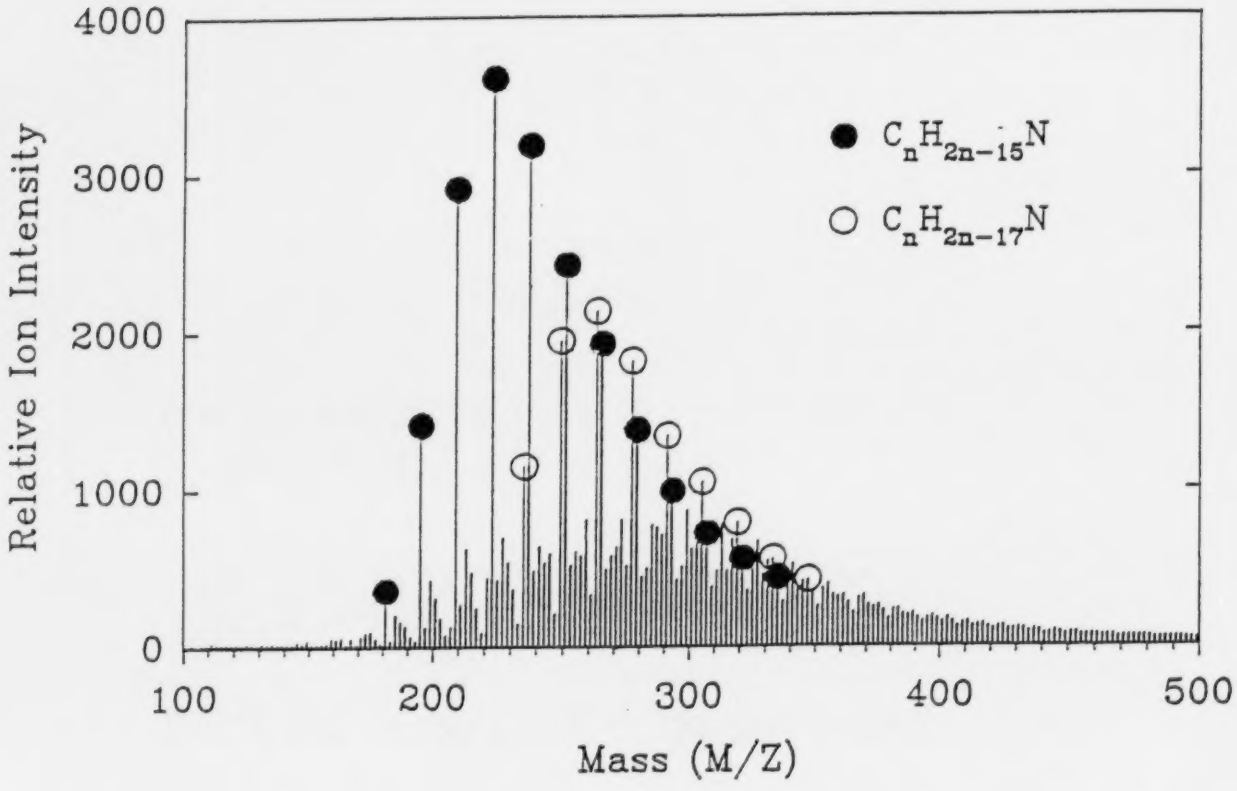


Figure 2.1 Field-ionization mass spectrum (FIMS) of methanol extract showing odd-mass ions.

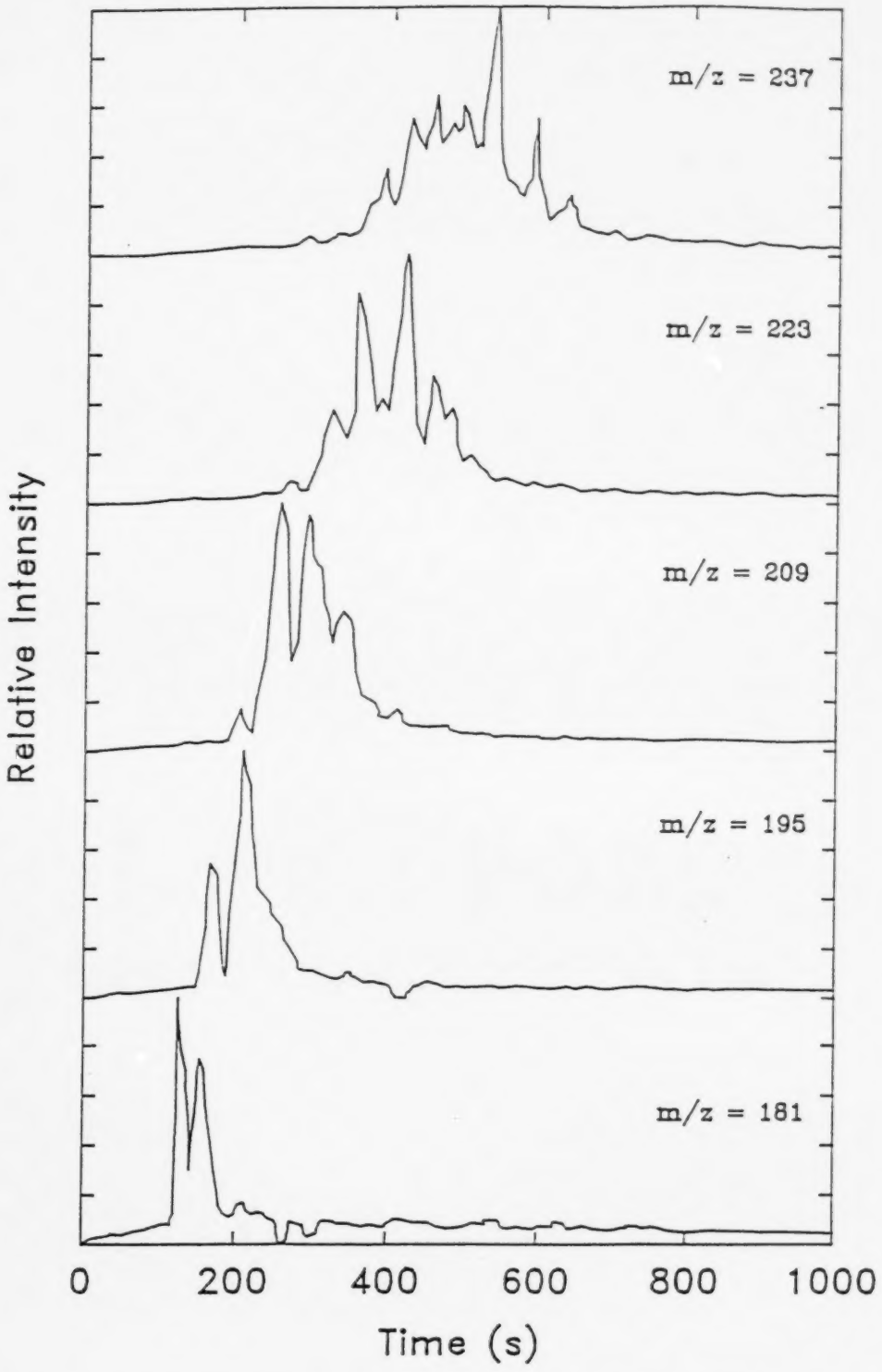


Figure 2.2 Cross scan of ions from carbazoles (m/z = 181, 195, 205 *etc.*) as a function of retention time by gc-ms.

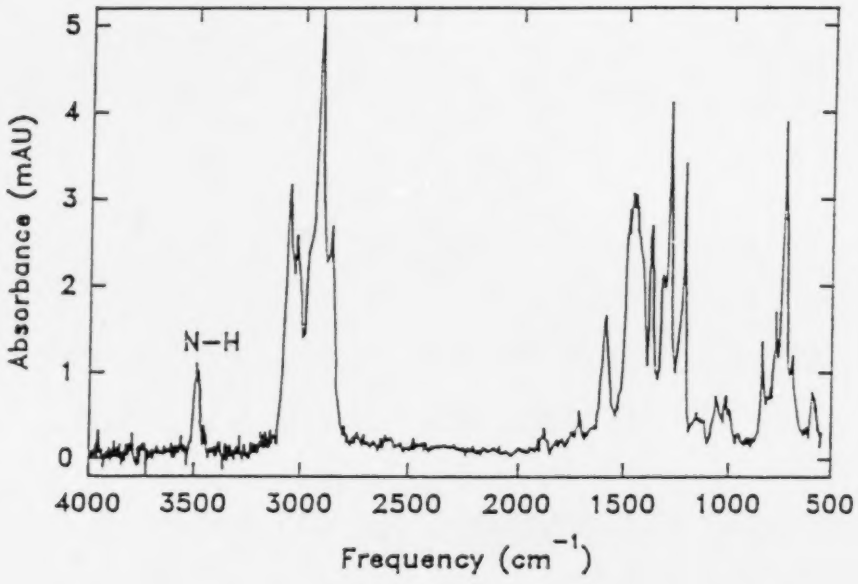


Figure 2.3 IR spectrum of gc peak showing the N-H band at 3501 cm^{-1}, and the bands due to aromatic hydrogens at 740, 800, and 848 cm^{-1}.

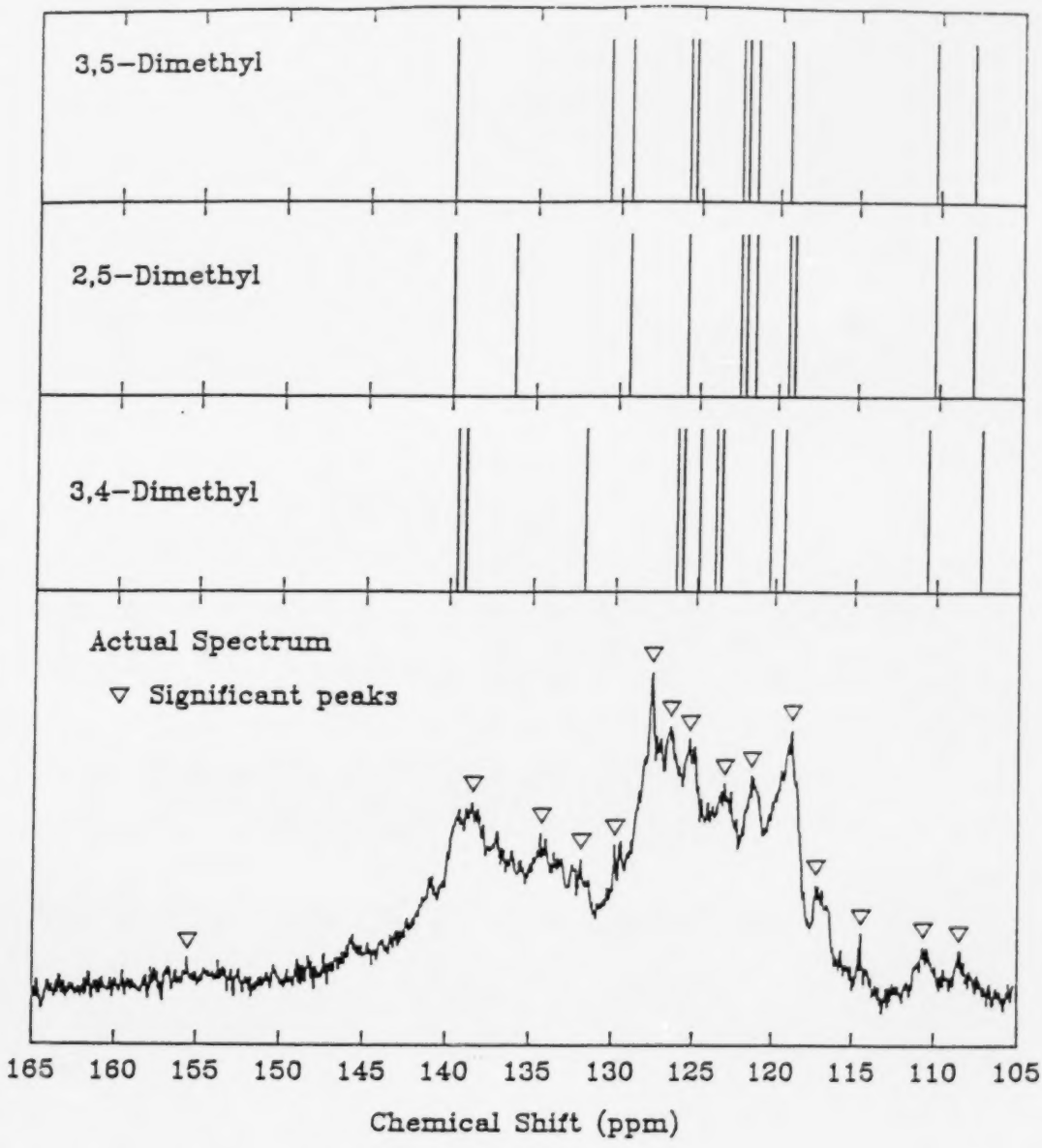


Figure 2.4 Signals due to aromatic carbons in the ^{13}C-nmr spectrum of the methanol extract, and calculated positions of signals from the most probable dialkylcarbazole isomers.

Chapter 3

Basic Nitrogen Compounds in Hydrotreated Gas Oil from Athabasca Bitumen[1]

INTRODUCTION

Nitrogen bases are ubiquitous in distillates derived from petroleum residues, heavy oils and coal liquids. Removal of these substituted pyridines, quinolines, and higher benzologs is required before the distillates can be blended into refinery feed stocks. Catalytic hydrodenitrogenation of quinoline has been intensively studied as a model for removal of nitrogen from hydrocarbon mixtures, and this literature has been summarized in recent reviews (Ho, 1988; Girgis and Gates, 1991).

Bitumen extracted from the Athabasca tar sands is used to produce a synthetic crude oil which constitutes about 15% of total Canadian oil production. Two main types of aromatic nitrogen compounds have been found in Athabasca bitumen: neutral pyrrole benzologs and basic pyridine benzologs (Mojelsky *et al.*, 1986; Frakman *et al.*, 1987). As shown in the previous chapter, alkyl-substituted carbazoles are the major type of neutral nitrogen compounds in synthetic crude oil derived from Athabasca bitumen . The present chapter focuses on the basic nitrogen compounds found in the same synthetic crude oil product. The objectives of this portion of the research were to recover gram quantities of nitrogenous material from a hydrotreated coker gas oil and to characterize the basic nitrogen components in the recovered materials.

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[1]A version of this chapter has been accepted for publication. Jokuty, P. L. and Gray, M. R. *Ind. Eng. Chem. Res.* **1992**.

EXPERIMENTAL METHODS

The oil was a commercially produced hydrotreated coker gas oil, derived from Athabasca bitumen. The material had been hydrotreated in a commercial trickle-bed reactor over a Ni/Mo on γ-alumina catalyst, at a temperature of 360-400 °C and a pressure of 9.5-11 MPa. A sulfur concentration of 4% in the coker gas oil ensured that the catalyst was completely sulfided.

Nitrogen compounds were retained by silica gel in a glass 100 cm x 3 cm o.d. column. The details of the frontal retention technique have been described in Chapter 2. The mass ratio of sample to sorbent was 9:1. One litre of oil was used. All solvents were of HPLC grade. A methylene chloride extract and a methanol extract were produced.

ANALYTICAL METHODS

For both extracts, C, H, N, and O were measured by the Microanalytical Lab, Chemistry Department, University of Alberta, using a Carlo Erba EA 1108 Elemental Analyzer. Sulfur was determined in a Leco S-132 Sulfur Determinator. For the oil, C, H, and S were determined as for the extracts. N was determined with an Antek pyroreactor and digital nitrogen analyzer.

Infrared spectra were recorded on a Nicolet 730 FTIR Spectrometer by co-adding 32 scans at a resolution of 4 cm^{-1}. The samples were dissolved in methylene chloride and run in 0.05 cm NaCl cells. GC-FTIR was performed by the Spectral Services Laboratory, Chemistry Department, University of Alberta, on a Hewlett-Packard HP5765 IRD using a Supelco Ultra 2 column. The temperature program was 150 °C for 2 minutes, then heating at 3 °C/min to a final temperature of 290 °C. A GC-mass spectrum of the methanol extract was obtained using a DB-1 column (0.25 mm i.d. x 30 m) coupled to a Varian VG 7070E mass spectrometer. This work was performed by L. Harrower, Mass Spectrometry Laboratory, Chemistry Department, University of Alberta. ^{13}C and ^{1}H

NMR spectra were obtained with a 300 MHz Bruker WH-300 spectrometer in the Nuclear Magnetic Resonance Laboratory, Chemistry Department, University of Alberta.

Potentiometric titration of basic nitrogen was carried out using a procedure similar to that of Buell (1967). Separate 90-100 mg samples were dissolved in 10 ml of benzene and 20 ml of either acetonitrile or acetic anhydride. Details of the titration procedure and sample calculations of the concentrations of weak bases and very weak bases are given in the Appendix.

RESULTS

The elemental analyses of the gas oil and extract fractions are given in Table 3.1. Other characteristics of the extract fractions are given in Table 3.2. The high sample to sorbent ratio of 9:1 gave only 61% recovery of total nitrogen, but the two solvent extracts were highly enriched in specific nitrogen types. Both extracts contained 3.8 wt % N. In the methylene chloride extract, 50% of the nitrogen was pyrrolic (determined by IR) and 16% was basic (determined by potentiometric titration). The infrared spectrum of the methanol extract showed no signal at 3500 cm^{-1}, therefore, the pyrrolic nitrogen content was negligible. Potentiometric titration of this fraction gave a single inflection point with a half-neutralization potential of 152 mV. This potential was typical of substituted pyridines and quinolines (Buell, 1967), so that this class accounted for 74% of the nitrogen in the sample. There was no evidence from the titration for stronger bases in the methanol extract. Because methanol would desorb even very polar compounds from the silica gel (Choi and Gray, 1991), these data indicated that primary, secondary, and tertiary alkylamines were absent from the synthetic crude oil. The methanol extract was highly enriched in nitrogenous bases; therefore, subsequent analysis concentrated on this fraction.

Nine types of ring systems containing a pyridine ring were identified by GC-MS analysis of the methanol extract (Figure 3.3.1). The largest peaks due to individual components were from C_9-pyridine and C_2- and C_3-tetrahydroquinoline. The relative

abundances of the different ring systems were estimated by summing base peak intensities as voltages (see Table 3.3). In all cases the base peak was considered to represent the molecular ion, M^+, if odd or $(M-1)^+$ if even. Only peaks with an intensity of at least 10% of the maximum were included. Using this method, the most abundant compounds were tetrahydroquinolines (THQ) and octahydrobenzoquinolines (OHBQ). Because the mixture did not contain any of the "stronger" weak bases (by potentiometric titration), the THQ and OHBQ were not hydrogenated in the nitrogen-containing ring. Furthermore, the mass spectra showed no evidence for elimination of HCN (mass = 27), which would be expected if cyclic amines were present. The isomers of THQ, therefore, were substituted 5,6,7,8-THQ, with an intact pyridinic ring. The MS fragmentation patterns indicated that multiple methyl substitutions were dominant, i.e. the base peaks had masses 14 units or more above the mass of the unsubstituted ring structure.

^1H and ^{13}C NMR spectroscopy of the methanol extract showed that the aromatic rings were highly substituted. The molar ratio of aromatic hydrogen to aromatic carbon was 0.23. A sharp signal at 6.8 ppm in the ^1H NMR spectrum (Figure 3.3.2) indicated that about 11% of the aromatic hydrogens were *meta* to the ring nitrogen (Chamberlain, 1974). This observation implied that the *meta* position was usually protonated rather than alkylated. The abundance of these *meta* protons also indicated that the pyridinic ring tended to be at the periphery of fused ring systems. This result was in agreement with the conclusion of Mojelsky *et al.* (1986) that the benzo(h)quinoline nucleus was probably the dominant structural unit for triaromatic ring systems in the basic nitrogen component of Athabasca maltene. The absence of a strong signal 150-160 ppm downfield of TMS in the ^{13}C NMR spectrum of the methanol extract indicated that the carbons *ortho* to the nitrogen were almost always substituted. IR spectra derived from peaks appearing at early retention times (6-15 minutes) in the GC-FTIR analysis of the methanol extract had a small peak at approximately 850 cm^{-1} (Figure 3.3) as expected from isolated hydrogen atoms in a polymethylpyridine (Katritzky and Ambler, 1963). The

absence of any overtone bands in the 2000-1650 cm^{-1} region was also consistent with polyalkyl-substitution of the pyridinic ring.

DISCUSSION

The basic nitrogenous components of Athabasca bitumen consist mostly of quinolines, benzoquinolines, and tetrahydrodibenzoquinolines (THDBQ) (Mojelsky *et al.*, 1986). Pyridines and THQ, if present, are insignificant in comparison to these other types of compounds. The oil used in this work was the product of coking followed by hydrotreating. Coking of the Athabasca bitumen may have caused some dehydrogenation of the nitrogen ring systems as well as some shortening of alkyl chains on the rings. Subsequent hydrotreating would definitely have resulted in hydrogenation of these ring systems. Therefore, the THQ, OHBQ, and octahydrodibenzoquinoline (OHDBQ) resulted from catalytic hydrogenation. Since pyridines were absent from the feed, in order for them to appear in abundance in the product they must have been formed by hydrogenation of higher benzologs to THQ, followed by cracking. Figure 3.4 shows the probable sequence of reactions for conversion of benzo- and dibenzoquinolines in the feed to THQ and alkylpyridines in the products. The most abundant number of carbons in substituents, in the bitumen and the product, is shown for each ring system. The hydrogenated ring systems had a low degree of substitution, i.e. THQ with C_2 substitution, OHBQ with methyl substitution. This observation would seem to indicate that on the whole, these ring systems tended to form from hydrogenation (possibly accompanied by some dealkylation) of ring systems present in the feed. On the other hand, completely aromatic ring systems (benzoquinolines, quinolines, and pyridines) showed a much higher degree of substitution suggesting formation primarily from the cracking of hydrogenated rings formed during hydrotreating. The pyridines would form from ring opening of THQ and OHBQ, and would be more extensively substituted. In summary, the distribution and degree of substitution of product ring types were consistent with a multistep mechanism for HDN,

including hydrogenation of carbon rings followed by cracking of the hydrogenated rings to give alkyl pyridines.

In contrast to a combination of hydrogenation and cracking reactions as in Figure 3.4, studies on HDN of quinoline as a model compound show the following dominant pathway (Ho, 1988):

$$\text{Quinoline} \xrightarrow{+2H_2} \text{1,2,3,4-THQ} \xrightarrow{+3H_2} \text{Decahydroquinoline} \xrightarrow{+2H_2} \text{propylcyclohexane} + NH_3$$

Shabtai *et al.* (1989) found a similar pathway for HDN of 5,6-benzoquinoline.

Both 1,2,3,4-THQ and decahydroquinoline are secondary amines, and are much more basic than quinoline. The present study found no evidence for such intermediates; instead, substituted 5,6,7,8-THQ was a significant component. This observation is consistent with the work of Claret and Osborne (1982) who found that alkyl substituents on the nitrogen-containing ring shifted the selectivity of the hydrogenation from 1,2,3,4-THQ to 5,6,7,8-THQ. For example, while catalytic reduction of unsubstituted quinoline yielded 100% 1,2,3,4-THQ, 2,4-dimethylquinoline yielded 80% 5,6,7,8-THQ.

The present study shows that the implications of substitution of the nitrogen ring go beyond the question of which ring is hydrogenated first. As illustrated in Figure 3.4, the accumulation of alkylpyridines suggests that the substituted nitrogen ring is resistant to conversion, and that cracking of saturated carbon rings is a significant pathway. These results may be relevant to any feed containing alkylated benzoquinolines, but the exact effects of alkyl substitution require further study. The substituted pyridine benzologs in synthetic crude oil appear to denitrogenate via a very different pathway from model studies of quinoline. If alkyl substitution strongly affects reaction pathways, as suggested by this study, then effective models for HDN should be based on the more resistant alkylquinolines and alkylbenzoquinolines. Furthermore, reaction networks should be studied at temperatures representative of commercial reactors. This study also indicates

that rate-limiting steps identified in model compound studies may not be relevant to the HDN of actual mixtures.

CONCLUSIONS

1. Alkyl-substituted tetrahydroquinolines and octahydrobenzoquinolines with an intact pyridinic ring are the most abundant basic nitrogen compounds found in synthetic crude oil.
2. These compounds were formed by catalytic hydrogenation of higher benzologs followed by cracking of the saturated hydrocarbon rings.
3. The substituted nitrogen ring is resistant to conversion and HDN of these pyridine benzologs appears to proceed via a different pathway from quinoline.
4. To effectively model HDN of complex feeds, the more resistant alkylquinolines and alkylbenzoquinolines should be used. Reaction temperatures should be representative of commercial reactors.

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Table 3.1

Elemental Analysis of

Hydrotreated Gas Oil and Extract Fractions

	Gas Oil		CH_2Cl_2 Extract		Methanol Extract	
	wt %	mol/100g	wt %	mol/100g	wt %	mol/100g
C	86.75	7.22	87.41	7.28	82.30	6.85
H	11.96	11.84	8.39	8.31	9.87	9.77
N	0.09	0.01	3.76	0.27	3.76	0.27
O	0.01*	0.00	0.10	0.01	2.87	0.18
S	1.20	0.04	0.34	0.01	1.21	0.04

* calculated from extract data

Table 3.2

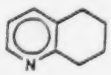
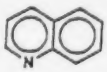
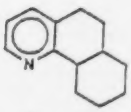
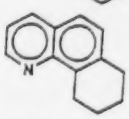
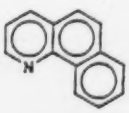
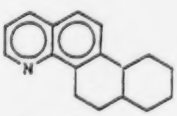
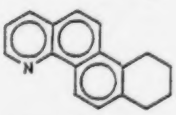
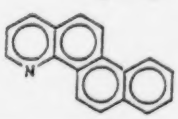
Characteristics of Extract Fractions

	CH_2Cl_2 Extract	Methanol Extract
Yield (g)	12.075	1.406
Yield (wt % of gas Oil)	1.33	0.15
Nitrogen (wt %)	3.76	3.76
Pyrrolic N (mol/100g)	0.14	0.00
Basic N (mol/100g)	0.046	0.21
^{1}H NMR	*	
Aromatic H (mol/100g)		0.61
Aliphatic H (mol/100g)		9.16
^{13}C NMR	*	
Aromatic C (mol/100g)		2.61
Aliphatic C (mol/100g)		4.24

Table 3.3

Relative Abundance of Ring Systems

in Methanol Extract

Ring System	Structure	Mole Percent of Identified Compounds*
Pyridine		12
THQ		34
Quinoline		13
OHBQ		29
THBQ		4
BQ		1
OHDBQ		4
THDBQ		2
DBQ		2

* Based on mass spectrometry by addition of base peak intensities assuming the same response factor for all nitrogen species.

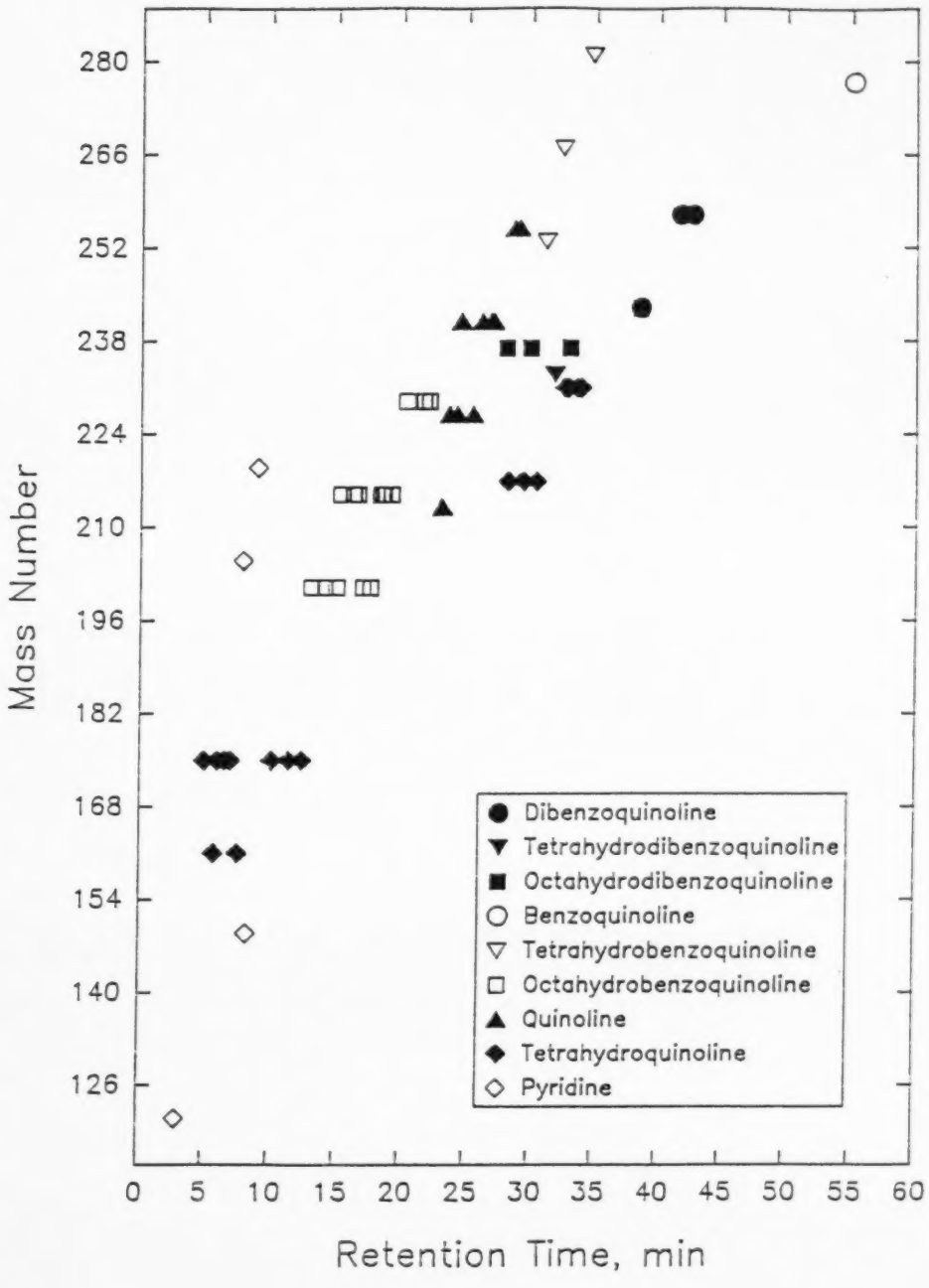


Figure 3.1 Ring systems identified by gc-ms analysis of the methanol extract.

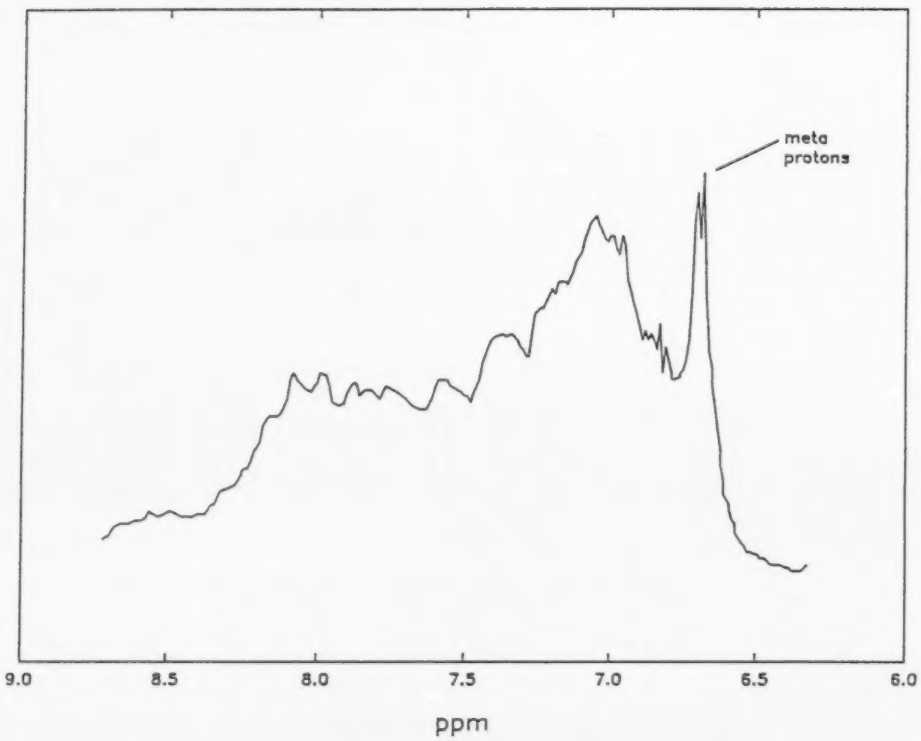


Figure 3.2 Aromatic portion of the ^{1}H-nmr spectrum of the methanol extract.

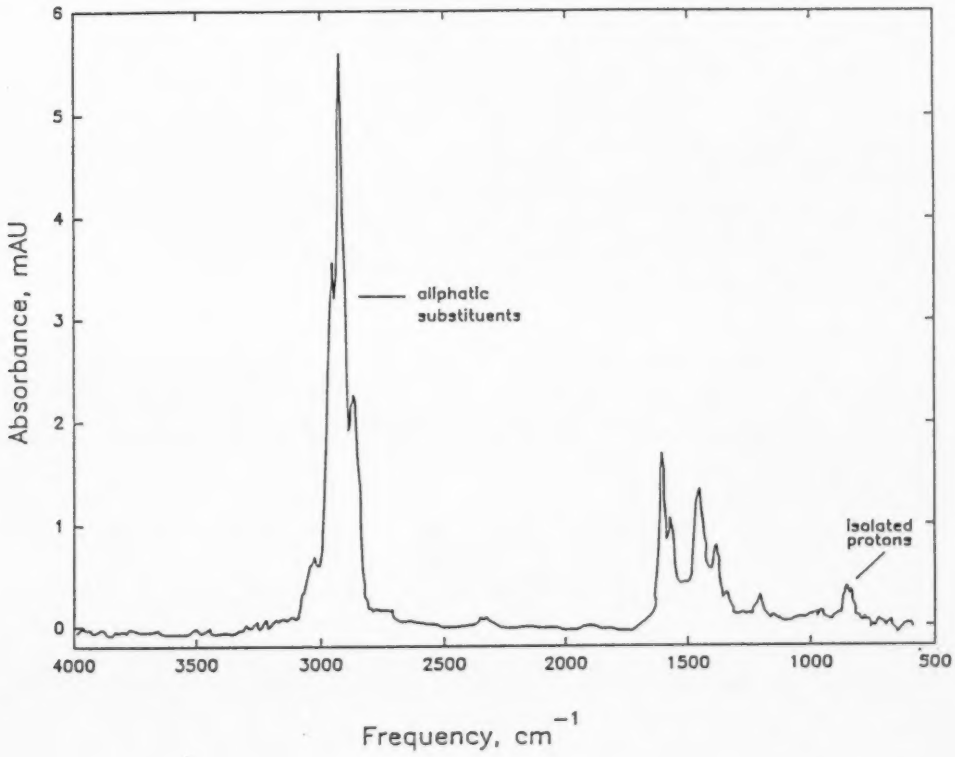


Figure 3.3 IR spectrum of the methanol extract at a gc retention time of 9.1 minutes.

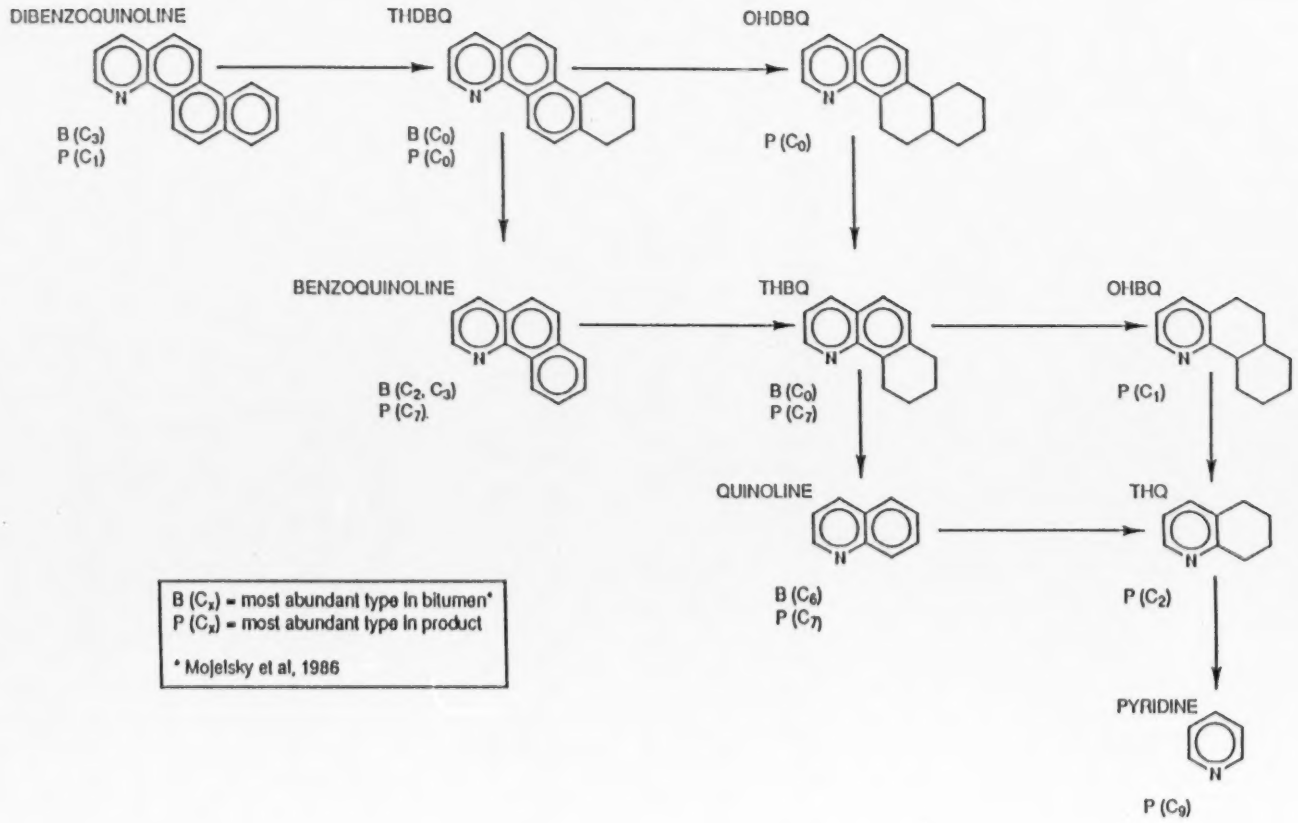


Figure 3.1 Ring systems identified by gc-ms analysis of the methanol extract.

Chapter 4

Structural Analysis of Catalyst Extracts

INTRODUCTION

Commercial hydrotreating catalysts can become deactivated by the accumulation of poisonous substances. Nitrogen compounds are particularly deleterious (Mills *et al.*, 1950). Nitrogen, oxygen, and sulfur species have been shown to accumulate preferentially on the surface of catalysts in service for only a few hours (Furimsky, 1978). Spent commercial hydrotreating catalysts also contained high concentrations of heteroatoms in solvent extracts (Choi and Gray, 1988). A detailed analysis of nitrogen compounds found in the basic fraction of catalyst solvent extracts was also given by Choi and Gray (1991). This paper reports on compounds found in the acid/neutral fraction of solvent extracts from two similar commercial hydrotreating catalysts. One catalyst was used for primary hydrotreating of a middle distillate from coker gas oil, and the other catalyst was used in secondary hydrotreating of the product oil from the first catalyst.

EXPERIMENTAL METHODS

Catalysts

Syncrude Canada Ltd. provided a spent middle distillate hydrotreating catalyst with the following characteristics:

- 3/16" x 3/32" Ni-Mo on γ-alumina catalyst (rings)
- a mixture of two catalysts, regenerated once and twice
- in service for 26 months

The catalyst sample was taken under nitrogen from the top of the reactor and put into a can which had been purged of air using dry ice.

Shell Canada provided a sample of spent gas oil hydrocracking catalyst with the following characteristics from the Scotford Refinery.

- 1/16" cylindrical extrudates, Ni-Mo on γ-alumina

This catalyst sample was also obtained and kept under nitrogen.

Solvents

Most solvents (*n*-pentane, methanol, methylene chloride) were HPLC grade from Fisher Scientific and were used as received. Ethylacetate, from Anachemia, was reagent grade and was distilled prior to use. Nitrogen was UHP grade from Medigas.

Extraction Method

To minimize exposure of the catalyst to oxygen, all handling of the catalyst, and the extraction itself were carried out under nitrogen. The catalysts were extracted using a Soxhlet extractor. A cellulose thimble was filled with catalyst and placed in the extractor. The condenser and solvent flask (with solvent) were then attached to the extractor. A small gas bag containing some nitrogen was fixed to the top of the condenser to prevent air infiltration and to accommodate expansion during heating of the solvent. All handling to this point was done inside a glove bag which had previously been purged repeatedly with nitrogen. The whole apparatus was then removed from the glove bag, and the extraction was begun. A heating mantle was used to boil the solvents.

The catalyst was extracted for 24 hours with n-pentane, 48 hours with methanol, and 24 hours with methylene chloride. The pentane extract was discarded and the methanol and methylene chloride extracts were combined. The solvents were removed by rotary evaporation, yielding Extract I. This extract had a very high ash content so it was back extracted with methylene chloride and filtered through a Whatman GF/C glass fibre filter to yield Extract II. An aqueous extract of the residue from this back extraction contained $NiSO_4$, an oxidation product, even though care had been taken to minimize exposure of the catalyst to oxygen. Extract II was extracted with 1 M HCl to remove

nickel salts, giving Extract III. Table 4.1 shows the yields and elemental analyses of Extracts I, II, and III.

In an attempt to separate the basic and acid/neutral components of Extract III, the sample was added to acidified silica gel and extracted overnight with methylene chloride to remove the acid/neutrals, and for approximately two hours with methanol to desorb the basic components (Choi and Gray, 1991). The overall recovery from the acidified silica gel separation was 98.1% for the Syncrude sample, with the acid/neutral fraction making up 94.7% and the base fraction 3.4%. Similarly, the Shell sample gave an overall recovery of 93.2%, with the acid/neutral fraction making up 91.8% and the base fraction accounting for 1.4%. The acid/neutral fractions from this procedure were called Syncrude AF and Shell AF. Table 4.2 shows the yields and elemental analyses of the acid and base fractions. A low resolution GC-MS analysis of the AF samples indicated abundant elemental sulfur, and contamination by phthalate esters and cyclosiloxanes.

A final separation of each acid fraction on silica gel was performed. This separation was intended to yield subfractions enriched in specific functional groups and to remove elemental sulfur as well as phthalate and siloxane contaminants from the samples. Approximately 40g of silica gel was packed into a glass column (2 cm i.d.) as a slurry in pentane. The AF sample was dissolved in a small amount of methylene chloride and added to the column. The sample was eluted from the column with a series of solvents of increasing polarity, i.e. *n*-pentane, methylene chloride, 5% ethylacetate in methylene chloride, 10% ethylacetate in methylene chloride, 5% methanol in methylene chloride, 10% methanol in methylene chloride, and methanol. 50 mL of each solvent or solvent mixture was used.

During the separation of Syncrude AF no distinct bands could be seen moving down the column so a large number of small (4 mL) fractions were collected. The first few fractions contained elemental sulfur. Gas chromatography was used to check the other fractions for cyclosiloxane and phthalate contamination. Some of these fractions

were subsequently combined to give Syncrude AFE (eluted early), Syncrude AFM (middle), and Syncrude AFL (eluted late). The Shell AF sample produced distinct bands as it was separated on the column and fractions were collected as the bands eluted. Two fractions were used for subsequent analyses, Shell AFE and Shell AFM. The Shell AFE sample was orange in colour, while the other AF subfractions were black. Table 4.3 shows the yields and elemental analyses of the Syncrude and Shell AF subfractions.

Analytical Methods

C, H, N, and O were determined as described in Chapter 3. Sulfur was also determined using the Carlo Erba EA 1108 Elemental Analyzer. Gas chromatograms, GC-mass spectra and infrared spectra were obtained as described in Chapter 2, but the samples for infrared spectroscopy were dissolved in carbon tetrachloride instead of methylene chloride to eliminate solvent absorption near 1200 cm^{-1}.

RESULTS

All steps up to the production of the Syncrude and Shell AF subfractions were necessary to eliminate interferences from catalyst oxidation products (nickel salts, sulfur) and contaminants introduced during the long extraction procedure (phthalate esters and cyclosiloxanes). For this reason, only results from the analysis of the AF subfractions will be discussed further.

Elemental Analysis

The Syncrude AFE and Shell AFE samples were both eluted with methylene chloride during the silica gel separation. Each accounted for approximately 4% of the corresponding AF sample (Table 4.3). However, the mass balance of the Shell AFE was significantly better than that of the Syncrude AFE, 96.3% compared to 87.5%. The oxygen and nitrogen contents of these two samples were nearly identical, but the H/C ratios were significantly different. The 1.1 H/C ratio of the Shell AFE indicates significant

aromatic content, while the 1.6 H/C ratio of the Syncrude AFE is typical of a more substituted and/or saturated hydrocarbon content. The C/O ratios of these two samples were in the same range, 22.5 for Syncrude AFE and 26.0 for Shell AFE. The nitrogen content of both the Syncrude AFE and the Shell AFE were very low, yielding correspondingly high C/N ratios of 655 and 503 respectively.

The Syncrude AFM sample was eluted with the 5% and 10% mixtures of methanol in methylene chloride. The yield of this fraction was 12.0% of the original Syncrude AF. The Shell AFM sample was eluted from the column with 5% methanol, and its yield, 12.3% of the AF sample, was nearly identical to that of the Syncrude AFM. The two AFM subfractions were both enriched in oxygen relative to the AFE subfractions. The C/N ratios of Syncrude AFM and Shell AFM were significantly different at 11.6 and 6.7 mol/mol respectively.

Syncrude AFL was eluted with pure methanol. While the C/O ratio was unchanged from that of the AFM sample, the C/N ratio dropped by 87% from 226 to 30. While the yield of the AFL subfraction was only 2.7% of the Syncrude AF, this fraction appeared to be even more enriched in nitrogen than Shell AFM by a factor of two.

Infrared Spectroscopy

The infrared spectra of the five AF subfractions are shown in Figures 4.1 to 4.5. The Syncrude AF subfractions all absorbed more strongly than the Shell AF subfractions. Each spectrum was obtained using an approximately equal mass of sample, however Shell AFE in solution was not as highly coloured as the other samples and Shell AFM did not dissolve completely. Syncrude AFL also did not dissolve completely, but the effect was more pronounced in the Shell AFM sample. This limited solubility in a nonpolar solvent was normal for samples with a high heteroatom content.

The spectra of Syncrude AFM (Figure 4.1), Shell AFE (Figure 4.2), and Shell AFM (Figure 4.3) will be discussed together, as they have several features in common. Peak assignments are from Silverstein *et al.* (1981).

Firstly, each of these spectra show a moderate to strong absorbance in the vicinity of 1700 cm^{-1}. In Syncrude AFM and Shell AFE the peak at 1705 cm^{-1} can be assigned to the carbonyl stretching of aliphatic and naphthenic ketones or carboxylic acid dimers. However carboxylic acids would also absorb at 1000-900 cm^{-1} and only a very weak absorbance is found in this region. In Shell AFM the carbonyl peak is shifted to 1695 cm^{-1} and there is a broad peak at 3200 cm^{-1}. Ketones containing both an alkyl and an aryl group could account for both of these absorbances.

Secondly, Shell AFE shows two peaks at 1773 cm^{-1} and 1738 cm^{-1} while Shell AFM shows one peak at 1772 cm^{-1} and Syncrude AFM has a slight shoulder at 1760 cm^{-1}. The higher frequency vibration is assigned to aromatic esters of carboxylic acids and the lower frequency is assigned to aliphatic esters. Each of the three spectra under discussion also displays a peak at approximately 1262 cm^{-1} which can be assigned to the C-O stretching vibration of esters. This peak is more pronounced in Shell AFE than in the other two spectra.

Thirdly, a broad peak at approximately 1600 cm^{-1} in both spectra is characteristic of aromatic ring stretching.

Lastly, the broad band of absorbances centred around 800 cm^{-1} could arise from the C-H bending modes of benzene derivatives or the C-H bending and ring bending modes of substituted furans (Silverstein *et al.*, 1981).

The remaining two spectra, those of Syncrude AFE (Figure 4.4) and Syncrude AFL (Figure 4.5), have in common a very weak carbonyl absorption. The spectrum of Syncrude AFE is similar to that of Shell AFE in containing ester peaks at 1770 cm^{-1} and 1261 cm^{-1}. The two spectra differ in that Syncrude AFE shows a very weak absorbance around 1600 cm^{-1} , confirming the less aromatic nature of the sample as indicated by its

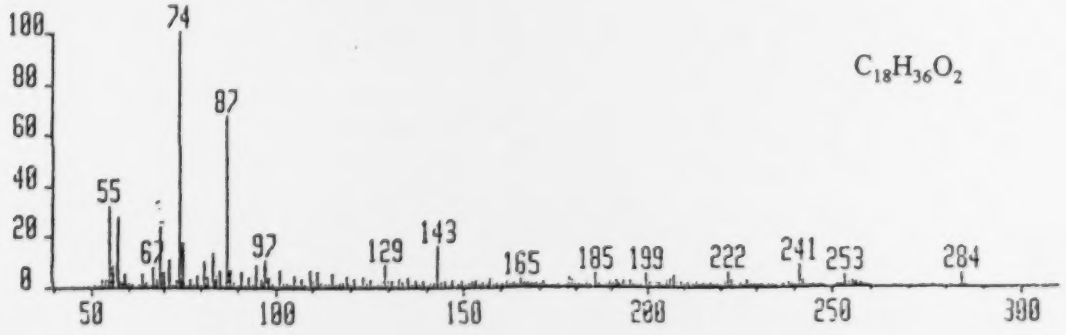
H/C ratio. Syncrude AFE also shows much less absorption around 800 cm^{-1} than Shell AFE.

The spectrum of Syncrude AFL contains several unique features, all indicating a high content of alcohols or phenols. Firstly, there is a broad underlying absorption from 3600-2400 cm^{-1}. This is typical of "polymeric" or hydrogen-bonded O-H groups. Secondly, two prominent peaks are found at 1208 cm^{-1} and 1154 cm^{-1}. These are characteristic of the alcoholic C-O absorbtion of saturated tertiary or highly symmetrical secondary alcohols. Thirdly, there is a sharp peak at 1033 cm^{-1} which is due to the alcoholic C-O stretch of several types of alcohols including tertiary, highly α-unsaturated alcohols such as phenols.

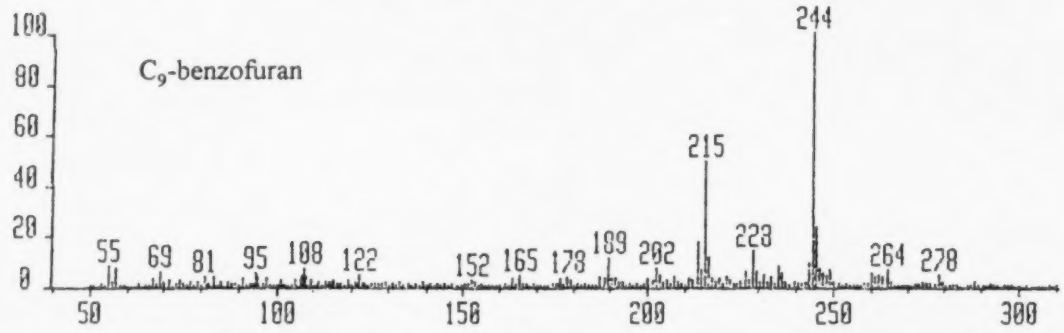
Mass Spectrometry

A low resolution GC-mass spectrum was obtained for each of the five AF subfractions. Of these, only the Shell AFE spectrum contained a large number of well resolved peaks, most of which could be assigned to four types of compounds. Peak assignments are from Silverstein *et al.* (1981).

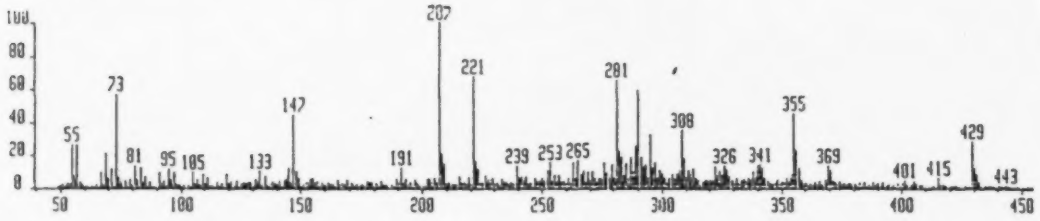
1. Methyl esters of aliphatic carboxylic acids from C_{16} to C_{30}. The mass spectra of this series of peaks show a small but distinct molecular ion peak (M^+). A peak at M-31, arising from the loss of O-CH_3, is diagnostic of methyl esters. The base peak is at m/e 74. This corresponds to the fragment resulting from McLafferty rearrangement and cleavage one bond removed from the C=O group. There is a series of peaks corresponding to $C_nH_{2n-1}O_2$.



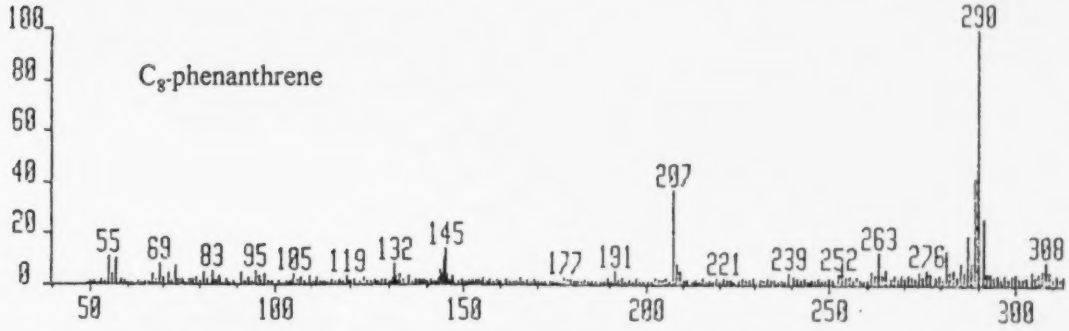
2. Furans (C_9-C_{13}) and benzofurans (C_8-C_{13}). The spectra of both furans and benzofurans contain a strong M^+ peak and a peak at M-29 due to loss of HCO. In the subtituted furan series there is a series of peaks resulting from loss of alkyl fragments. In the benzofuran series, much less alkyl fragmentation is evident.



3. Trihydroxybenzophenanthrene or C_{24} substituted phenol. Three strong peaks in the total ion chromatogram of Shell AFE displayed mass spectra consistent with these compounds. There is a distinct M-1 peak at m/e 429, which is accompanied by three peaks differing by 74 mass units (m/e 355, 281, 207). These three peaks are more easily accounted for in trihydroxybenzophenanthrenes than in the substituted phenol. They would result from the consecutive loss of an olefin plus water. Only one such loss would be possible from a monohydroxy compound such as phenol. Both types of compounds could account for the prominent peak at m/e 73. This would be due to formation of $[RR'COH]^+$ where $R=CH_3$ and $R'=CH_2C$. Small peaks due to loss of CO and CHO are also found.



4. Phenanthrenes (C_7-C_9). These compounds elute late in the chromatogram but are well resolved from the background. The C_7-phenanthrene peak is the most intense peak in the total ion chromatogram. The mass spectra of this series show a strong M^+ peak and very little fragmentation. This would tend to indicate multiple methyl substitution, as α-methyl groups do not cleave easily from the aromatic nucleus.



The GC-mass spectra of Syncrude AFE, Syncrude AFM, and Shell AFM contain few resolved peaks. Syncrude AFE shows evidence of a series of furans with C_9-C_{12} substitution. Syncrude AFM, Shell AFM and Syncrude AFL all contain the same late-eluting aromatic hydroxyl compounds as Shell AFE. The GC-mass spectrum of Syncrude AFL also contains some peaks which could be assigned to C_2- and C_4- substituted octahydrobenzocarbzoles. These mass spectra contain a distinct M^+ peak, and complex fragmentation patterns consistent with fragmentation of the hydrogenated rings.

DISCUSSION

While the oil-derived polar materials of Chapters 2 and 3 were quite amenable to structural analysis, the same cannot be said of the material extracted from the spent hydrotreating catalysts. The mass balances of all but the Shell AFE subfraction were very low, ranging from 78.61% in Shell AFM to 89.75% in Syncrude AFM. These totals do not include sulfur content, but it would be unlikely to exceed 5% in any of the subfractions given that elemental sulfur recovered during the silica gel separation accounted for

approximately half of the sulfur content of both Syncrude AF and Shell AF. In any case, none of the infrared spectra of the AF subfractions showed any clear evidence for sulfur-containing functional groups.

Based on the work described in the previous chapters and the earlier work of Choi and Gray (1988), it was anticipated that the catalyst extracts would have high nitrogen and oxygen contents. The poor mass balances necessitate the use of C/N and C/O ratios for comparison purposes. Choi and Gray (1988) obtained a gas oil catalyst Extract II in the same manner used in the current work. The C/N and C/O ratios of this fraction were 25.1 and 5.1 respectively. This compares to 90.8 and 4.8 for the same ratios in Syncrude Extract II. The difference in C/N ratios is reasonable, given that Choi and Gray (1988) used a gas oil hydrotreating catalyst, and the current work was done on a middle distillate hydrotreating catalyst. The gas oil may be expected to have a nitrogen content 3-4 times that of the middle distillate (Gray, 1990).

As can be seen from Table 4.2, the relative nitrogen content is highest in Extract I and declines steadily with each subsequent extraction. The relative oxygen content shows the same decline. The Syncrude AF produced from the separation of Syncrude Extract III on acidified silica gel showed a 15% decrease in nitrogen relative to Syncrude Extract III. The oxygen content was essentially unchanged. Shell AF showed a 5% decrease in nitrogen and a 17% decrease in oxygen relative to Shell Extract III. At the same time, both Syncrude BF and Shell BF had a two-fold increase in nitrogen. The oxygen content of Syncrude BF was unchanged, while that of Shell BF decreased by 11.5%. It is unclear how the relative oxygen content of both Shell AF and BF could decrease relative to Shell Extract III.

The purpose of the acidified silica separation was to remove the basic components of the catalyst extract, as these had already been thoroughly analyzed (Choi and Gray, 1991). The yield of Syncrude BF relative Extract II was 2.1% comparable to 3.2% total

base fraction found by Choi and Gray (1991). Again, the lower base content found in the current study may reflect a lower nitrogen content in the feed oil.

The data from infrared spectroscopy and mass spectrometry of Shell AFE agree quite well. The series of methyl esters, furans, and benzofurans detected by GC-MS agree with peak assignments in the infrared spectrum. There is no clear infrared assignment to support the finding of hydroxyl compounds by GC-MS, but this could be due to their limited abundance and/or degree of substitution. The phenanthrenes would not be expected to show any characteristic absorbances in the infrared beyond aromatic ring stretching and possibly ring substitution patterns if specific isomers were suitably abundant. To this extent the infrared spectrum does not preclude the presence of phenanthrenes.

The limited mass spectral data obtained from the other AF subfractions also supports peak assignments in the infrared spectra of those fractions. For instance, the hydroxyl-containing series of Syncrude AFM and AFL could account for the broad, underlying, hydroxyl absorbance observed in both infrared spectra. Octahydrobenzocarbazoles were identified in the GC-MS of Syncrude AFL. The absence of any absorbance near 3500 cm^{-1} indicates that these must be N-substituted and/or in low abundance.

While the infrared and mass spectral data of the AF subfractions tend to support each other, they do not answer the question "Where did these compounds originate?". Dibenzofurans have been identified in Athabasca bitumen (Selucky *et al.*, 1977). It is possible that the furans and benzofurans found in the AF subfractions are "remnants" of dibenzofurans originating in the bitumen. Aromatic compounds containing four rings have been identified in Athabasca maltene (Payzant, *et al.*, 1985a) and tetra- and pentaaromatics were identified in Athabasca bitumen (Selucky *et al.*, 1977). These compounds could give rise to the phenanthrenes found in Shell AFE. Octahydrobenzocarbazoles (OHBC), found in Syncrude AFL, may be derived from

benzocarbazoles which have been identified in Athabasca maltene (Payzant *et al.*, 1985b). OHBC's were not among the neutral nitrogen compounds identified in Chapter 2, but tetrahydrobenzocarbazoles (THBC) and tetrahydrocarbazoles (THC) were. This suggests that THBC's hydrogenate at a slower rate than OHBC's crack.

The methyl esters and hydroxyl compounds identified in this study would not be expected to survive reaction conditions in a commercial hydrotreating unit, therefore they must be oxidation products which were formed outside of the reactor. Emanuel *et al.* (1967) have written extensively on the liquid-phase oxidation of hydrocarbons. They believe that on the whole, the mechanism of the chain oxidation of hydrocarbons can be represented in the following way:

(0) $RH \xrightarrow{O_2} \dot{R}$ (origin of the chains)

(1) $\dot{R} + O_2 \rightarrow R\dot{O}_2$ (propagation of the chains)

(2) $R\dot{O}_2 + RH \rightarrow ROOH + \dot{R}$

(3) $ROOH \rightarrow R\dot{O} + \dot{O}H$ (degenerate branching)

(4) $\dot{R} + \dot{R} \rightarrow R\text{–}R$ (termination of the chains)

(5) $R\dot{O}_2 + \dot{R} \rightarrow ROOR$

(6) $R\dot{O}_2 + R\dot{O}_2 \rightarrow ROH + R_1COR_2 + O_2$

Therefore, the alkanoic methyl esters observed in Shell AFE are methylated carboxylic acids formed by oxidation of long alkyl chains and subsequent methylation during the long extraction with methanol. Mojelsky *et al.* (1992) found a similar series of *n*-alkanoic acid methyl esters after Ruthenium ions catalyzed oxidation (RICO) of Athabasca asphaltenes. They observed alkyl chains from 5 to 25 carbons in length, significantly shorter than the 16 to 30 carbon alkyl chains observed in Shell AFE.

The hydroxyl compounds found in Shell AFE and AFM, and Syncrude AFM and AFL likely were formed by oxidation of side chains, although hydroxyl compounds were identified in Athabasca maltene (Payzant *et al.*, 1985b).

CONCLUSIONS

1. Methyl esters of alkanoic acids, furans, benzofurans, and phenanthrenes are the most abundant compounds identified in material extracted from a spent secondary hydrotreating catalyst.
2. Furans and octahydrobenzocarbazoles are present in material extracted from a spent primary hydrotreating catalyst.
2. Oxidation of the material adsorbed to the catalyst occurs readily upon exposure of the catalyst to air.

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Table 4.1

Analysis of Extracts I, II, and III

Sample	Yield wt %	C wt %	H wt %	O wt %	N wt %	S wt %	CHONS wt %	H:C mol/mol	C:O mol/mol	C:N mol/mol
Sync. Ext. 1	2.9%	25.70	4.94	32.01	1.05	5.47	69.17	2.3	1.1	28.6
Sync. Ext. 2	1.0%	56.82	7.95	15.92	0.73	8.97	90.39	1.7	4.8	90.8
Sync. Ext. 3	0.6%	69.74	9.20	6.43	0.66	9.05	95.08	1.6	14.5	123.3
Shell Ext. 1	4.3%	14.80	3.85	38.48	0.27	11.15	68.55	3.1	0.5	64.0
Shell Ext. 2	0.3%	56.71	6.14	13.01	1.06	6.14	83.06	1.3	5.8	62.4
Shell Ext.3	0.2%	67.82	7.35	8.70	1.08	4.51	89.46	1.3	10.4	73.3

Table 4.2

Analysis of AF and BF

Sample	Yield wt %	C wt %	H wt %	O wt %	N wt %	S wt %	CHONS wt %	H:C mol/mol	C:O mol/mol	C:N mol/mol
Sync. A.F.	94.7%	68.43	9.12	6.40	0.55	8.38	92.88	1.6	14.3	145.2
Sync. B.F.	3.4%	65.91	8.87	6.17	1.19	4.74	86.88	1.6	14.2	64.6
Shell A.F.	91.8%	66.15	7.26	7.25	1.00	4.70	86.36	1.3	12.2	77.2
Shell B.F.	1.4%	55.86	6.92	6.44	1.54	1.67	72.43	1.5	11.6	42.3

Table 4.3

Analysis of AF Subfractions

Sample	Yield wt% of AF	C wt %	H wt %	O wt %	N wt %	CHON wt %	H:C mol/mol	C:O mol/mol	C:N mol/mol
Sync. AFE	4.2%	73.29	9.72	4.34	0.17	87.52	1.6	22.5	503.0
Sync. AFM	12.0%	71.70	9.47	8.21	0.37	89.75	1.6	11.6	226.1
Sync. AFL	2.7%	63.12	9.31	7.18	2.47	82.08	1.8	11.7	29.8
Shell AFE	4.0%	84.26	7.59	4.32	0.15	96.32	1.1	26.0	655.4
Shell AFM	12.3%	59.55	5.99	11.89	1.18	78.61	1.2	6.7	58.9

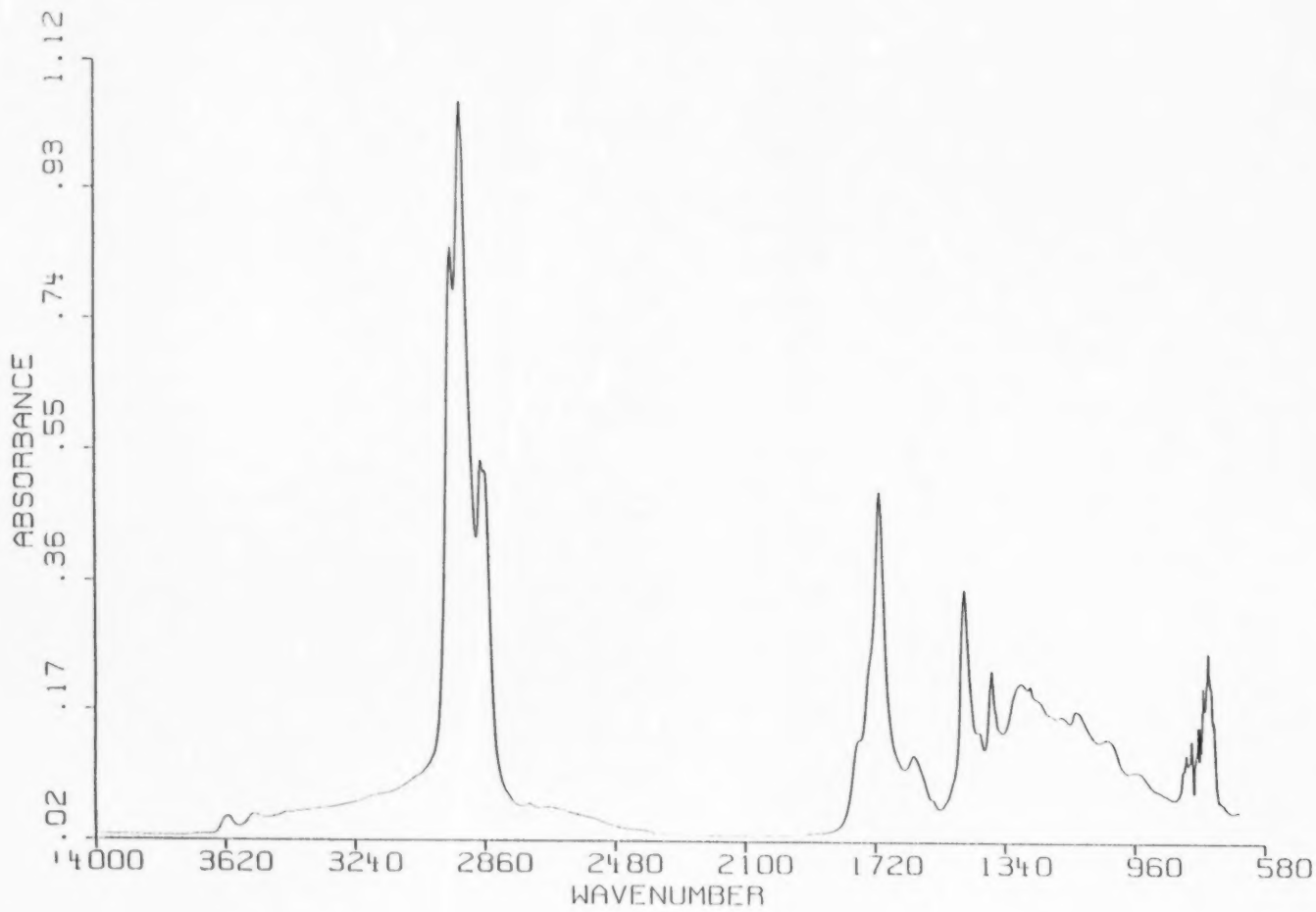

Figure 4.1 IR spectrum of Syncrude AFM.

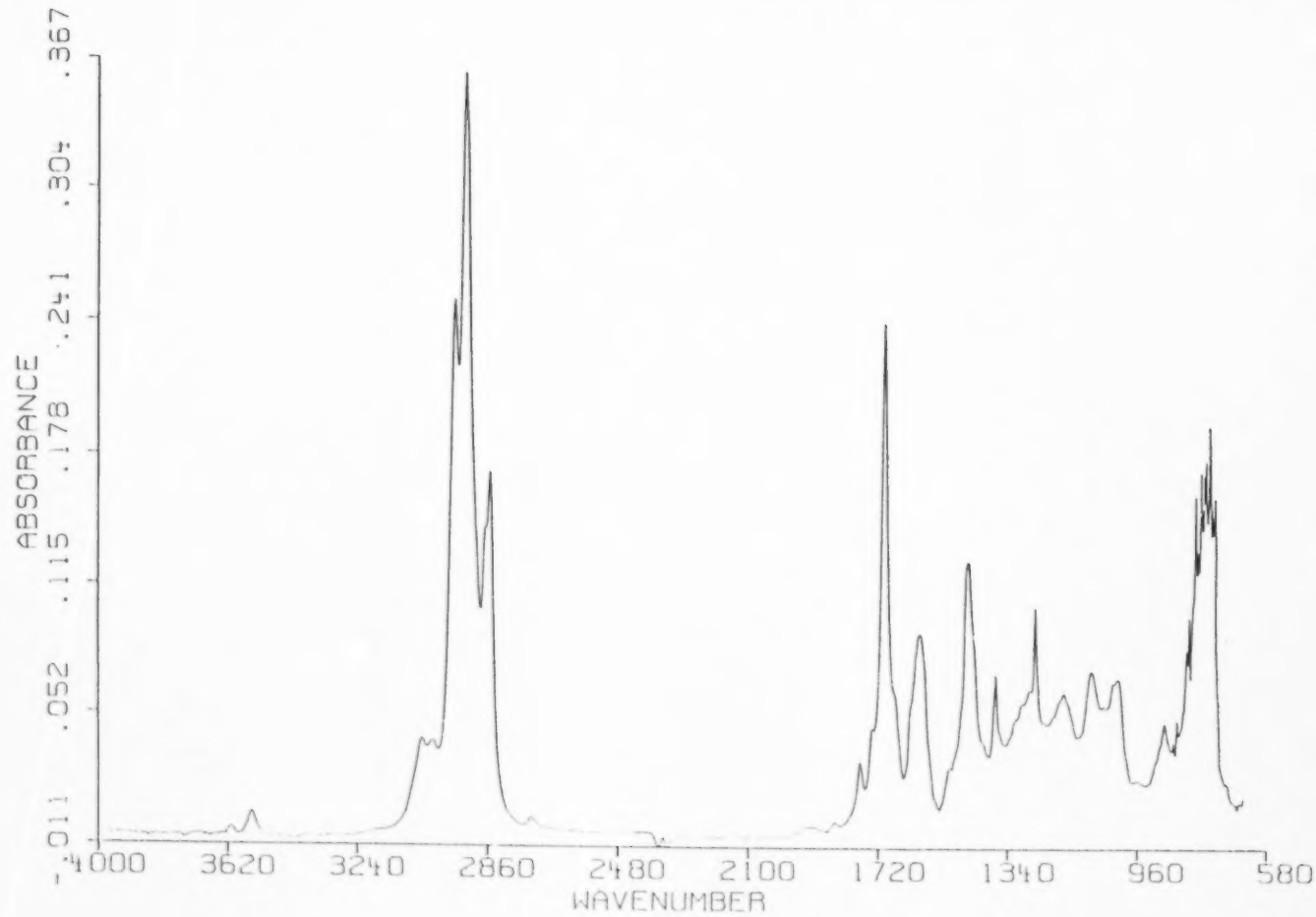

Figure 4.2 IR spectrum of Shell AFE.

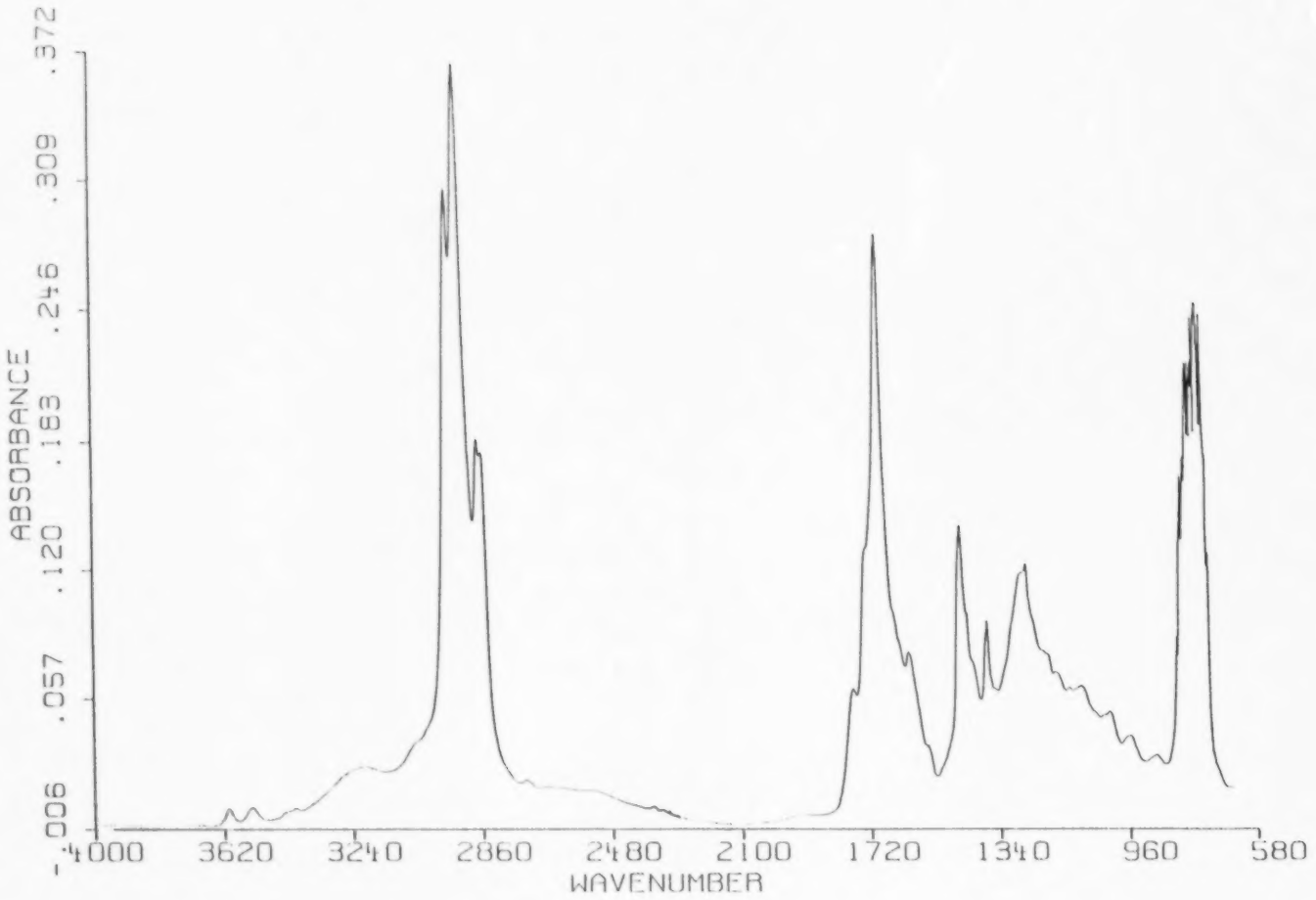

Figure 4.3 IR spectrum of Shell AFM.

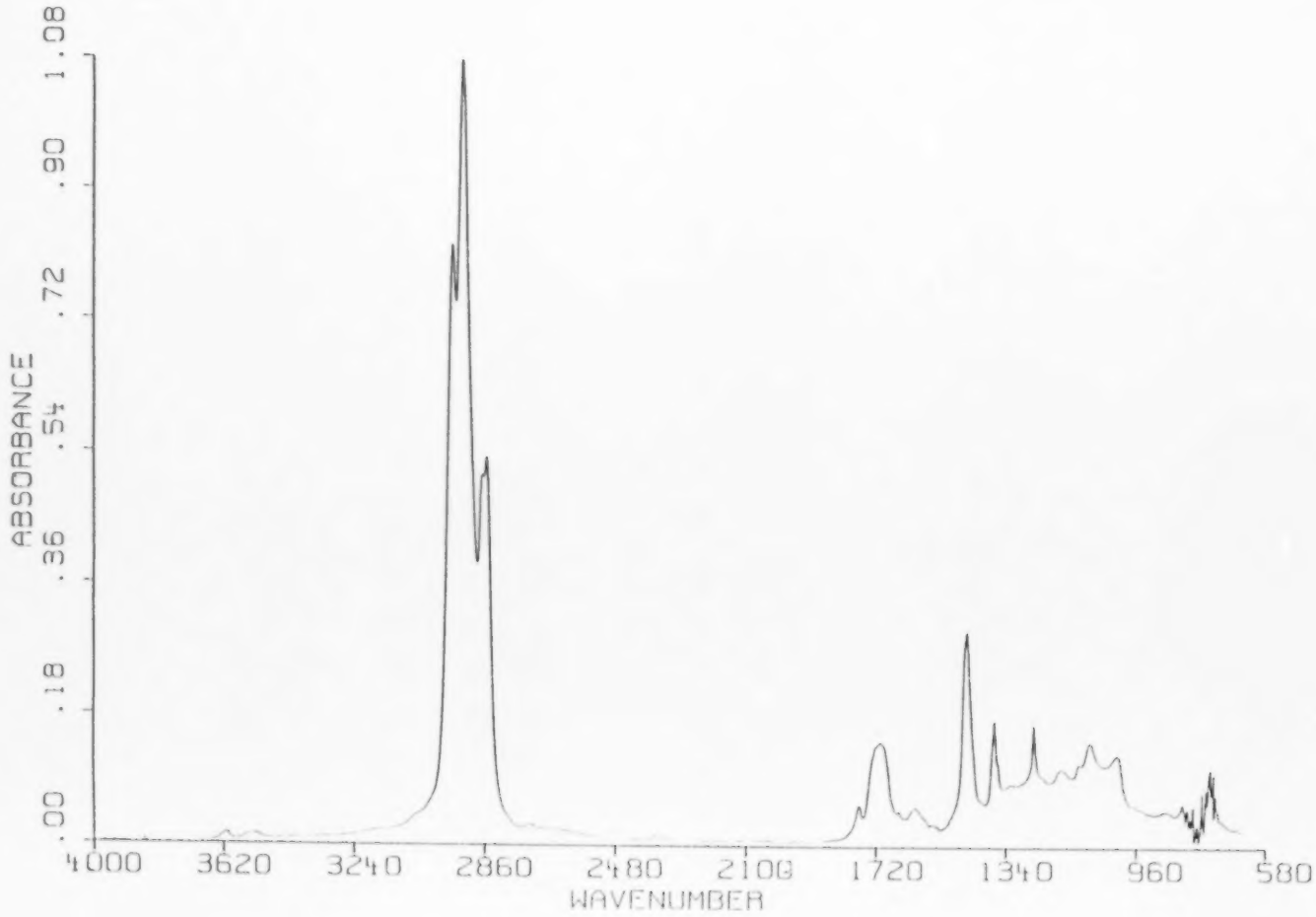

Figure 4.4 IR spectrum of Syncrude AFE

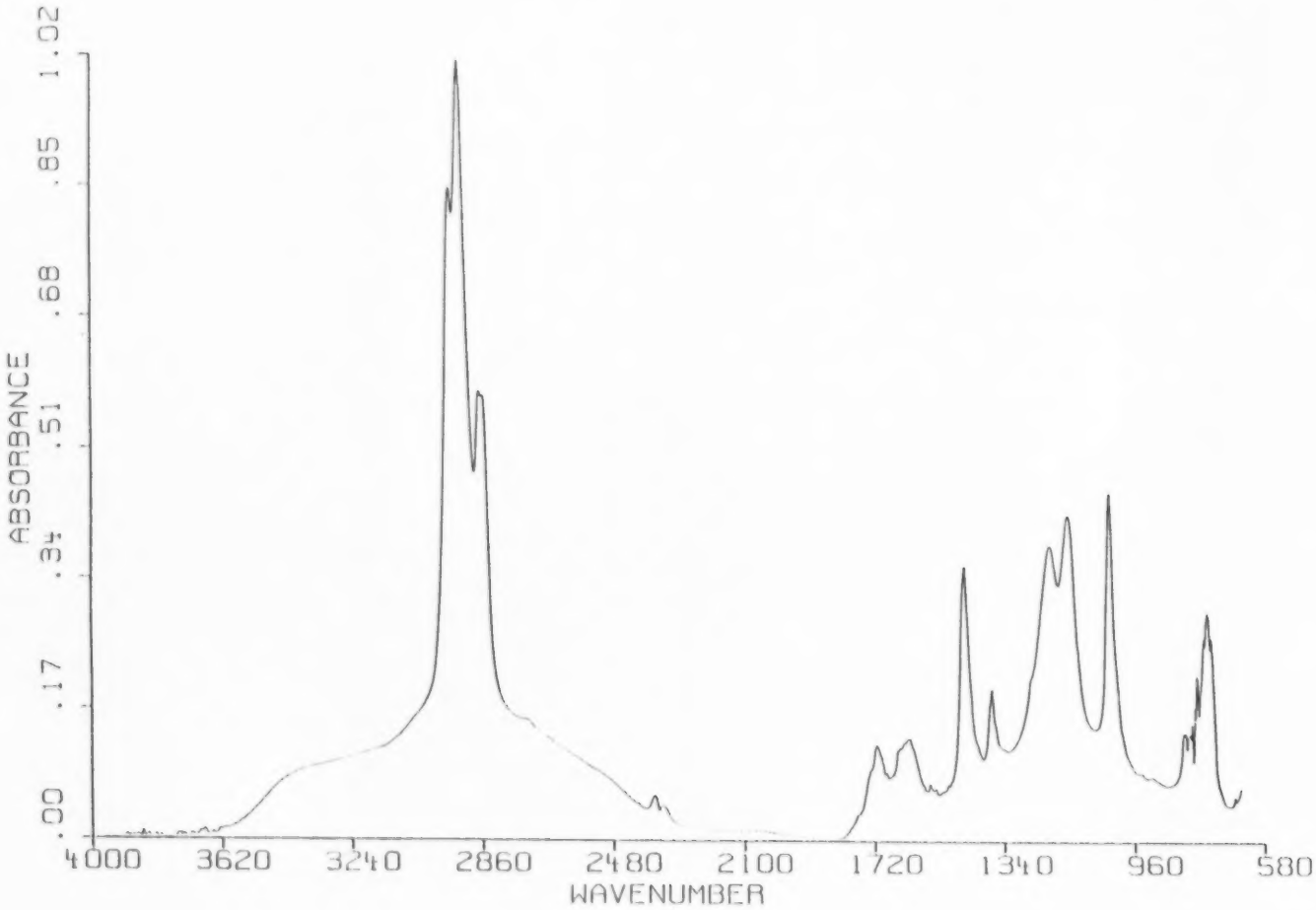

Figure 4.5 IR spectrum of Syncrude AFL.

Chapter 5

Conclusions

The retention chromatographic method developed in this work was very effective for concentrating the polar compounds from the oil. Future work could employ this technique to recover gram quantities of polar material from lighter distillate fractions such as naphtha.

Spectroscopic techniques (IR, NMR) were very useful in characterizing the nitrogenous material from the hydrotreated coker gas oil. These techniques allowed the elucidation of ring types and in some cases substitution patterns of the neutral and basic compounds from the oil.

Solvent extraction of spent hydrotreating catalysts can provide gram quantities of extracted material. In order to make good use of spectroscopic techniques and mass spectrometry, more effective methods of fractionation must be employed. However, these methods will be of little practical use unless oxidation of the catalyst can be prevented. The development of these methods remains for future study.